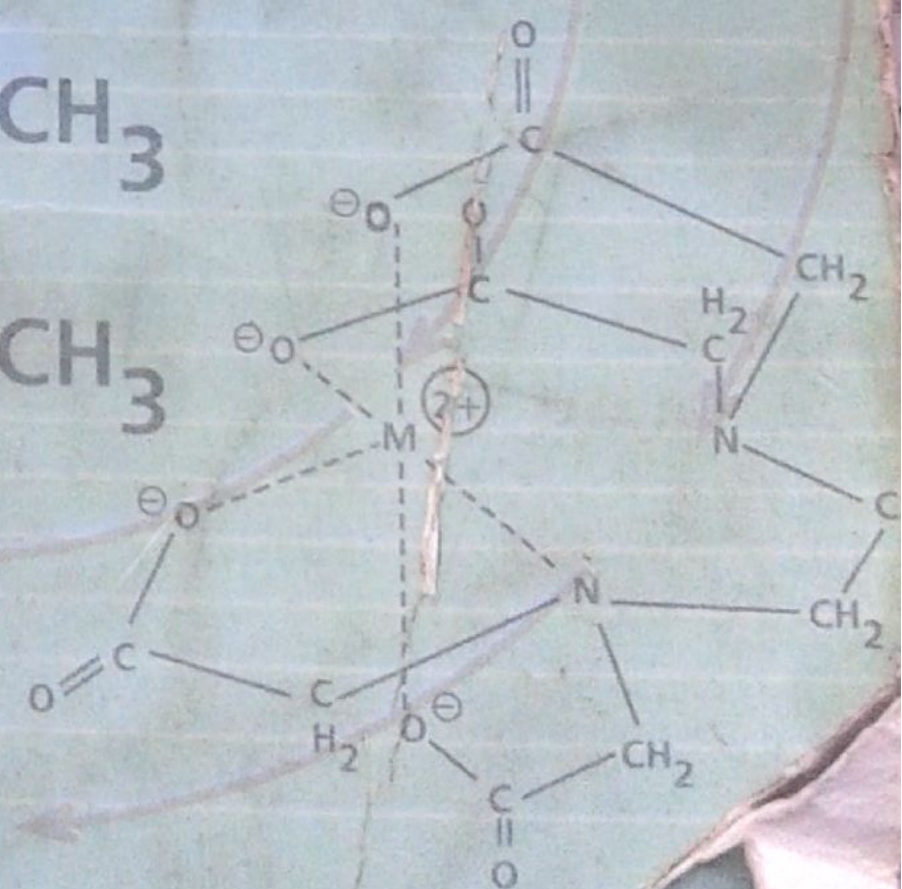
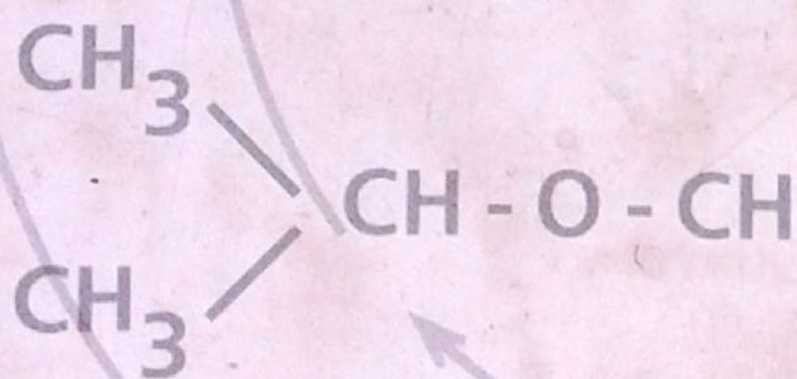
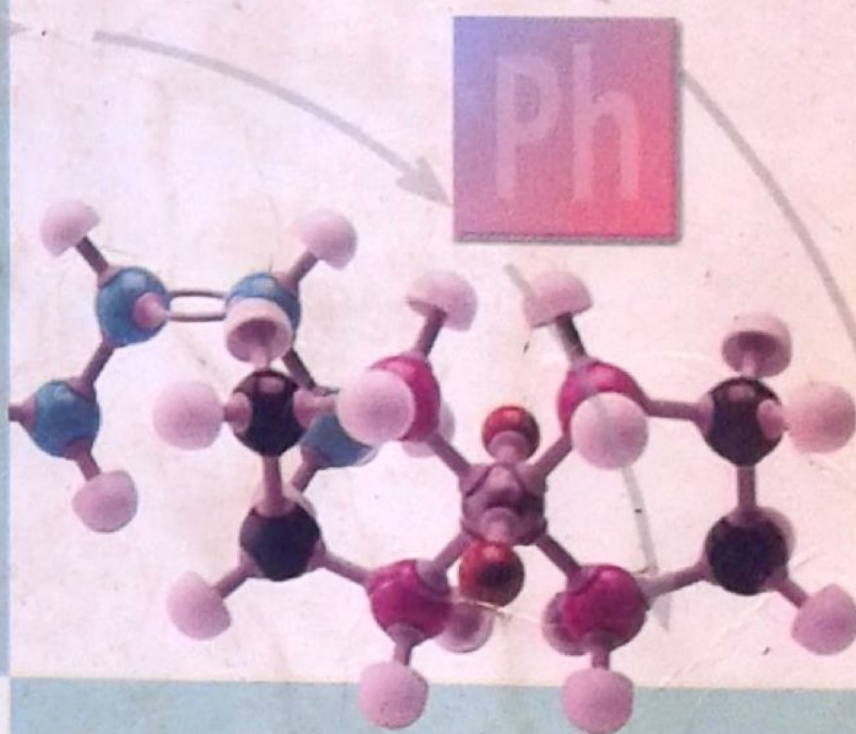
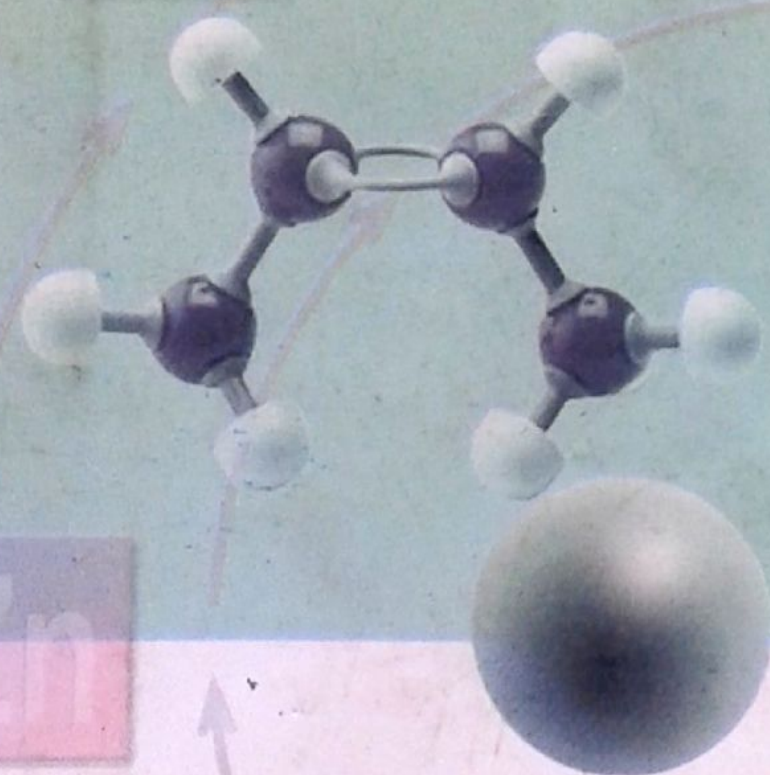


As per R.G.P.V., Bhopal, (M.P.)

# Theory & Practicals of **ENGINEERING CHEMISTRY**

Theory & Practicals of **ENGINEERING CHEMISTRY**

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# THEORY AND PRACTICALS *of* ENGINEERING CHEMISTRY

As per the latest syllabus of RGPV for the year 2010-11

Rajiv Gandhi Proudyogiki Vishwavidhalaya,  
BHOPAL (M.P.)



By

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# Preface To The Fifth Edition

This thoroughly revised and updated edition completely covers the latest theory & practical syllabus of Engineering Chemistry course offered to first year B.E./B.Tech. students of **Rajiv Gandhi Proudyogiki Vishwavidhalaya, Bhopal (M.P.)**

*The following have been included in this edition :*

- Large number of examples (well integrated into the body of the text as well as at the end of each chapter in sections of solved examples) gives students manifold opportunities to understand the topics being presented.
- Many solved numericals are spread throughout the book that give students a chance to see how problems can be worked out.
- The utility of the book has been enhanced with new figures to promote visual, spontaneous learning.
- Emphasis has been placed on *case studies and applications* for explaining the usefulness of various topics.
- The complete coverage of experiments as per the latest RGPV syllabus has also been included.

*The book aims at :*

- Imparting intensive and extensive knowledge of the subject so that readers can understand the role of chemistry in the field of engineering,
- Developing analytical capabilities of students so that they can characterize, transform and use materials in engineering and apply knowledge gained in solving related engineering problems,
- Developing the habit of scientific reasoning in the students so that they can work with open and inquiring mind.

*Salient features of the book are :*

- Offers easy, compact and accurate study material.
- Independent, up to date and complete coverage of various topics in almost all the chapters.
- Simple, systematic and logical development of the subject with emphasis on the underlying fundamental concepts, principles and applications.
- Incorporates thought stimulating exercises, latest examination questions and Numerical problems (with answers for self assessment).
- Incorporates Question Bank and Solution.
- Incorporates latest RGPV Examination Papers and Solution.
- Incorporates suggestions from students and advice from reputed faculty members.
- Enables you to perform effectively and with confidence in the exams.

I hope this book will serve its purpose and prove beneficial to its readers. Any suggestions and constructive criticism towards the further improvement of the book are most welcome.

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One of the main sources of inspiration for writing this book has been the many interested students in my classes.

This book is based mainly on the lecture notes I prepared for the B.E./B.Tech and M.Sc. classes on the subject and on the tutorial discussions with the students at Amity School of Engineering and Technology (ASET), Lingaya's Institute of Management & Technology (LIMAT) and Jamia Millia Islamia (JMI). I am grateful to all the authors of the books I have used in preparing the notes.

I express my sincere gratitude to **Dr. Ashok K. Chauhan**, founder President, 'Amity Universe', and **Mr. Atul Chauhan**, President, RBEF and 'Amity Universe' for their constant inspiration and encouragement.

I am thankful to **Prof. B. P. Singh**, Director, Amity School of Engineering and Technology; and **Prof. D. P. Tiwari**, Director, Amity School of Engineering for their continued guidance and encouragement.

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Each one and many more have boosted my confidence to serve the academic community much better. It has been a pleasure to work with all of them. I am grateful in measure beyond words, and have learned a lot from their wise advice.

I deeply acknowledge my parents for their never ending encouragement, moral support, patience and understanding during the preparation of this book. It is my sincere pleasure to thank my wife, **Mrs. Taruna Chawla** for editing & moral support.

I wish to thank the Publisher for the sustained interest shown by him during the entire work. A sincere expression of thanks goes to the entire staff of Dhanpat Rai and Company (Pvt.) Ltd.

Generous participation of faculties and students to eliminate errors in the text and to refine the presentation will be greatly acknowledged.

(SHASHI CHAWLA)

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*Dedicated to  
my mother, Mrs. Santosh Chawla  
for her support, enthusiasm, unfailing  
cooperation and inspiration*



# SYLLABUS

## BE 101 (Common for all Branches) From Session 2010-2011

Branch : Common Semester

Course: BE101 Engineering Chemistry

Credit : 4 + 2

### Unit I

#### WATER AND ITS INDUSTRIAL APPLICATIONS

Sources, Impurities, Hardness and its units, Industrial water characteristics, softening of water by various methods (External and Internal treatment), Boiler trouble causes, effect and remedies, Characteristics of municipal water and its treatment, Numerical problems based on softening methods.

### Unit II

#### FUELS AND COMBUSTION

Fossil fuels and classification, Calorific value, Determination of calorific value by Bomb calorimeter Proximate and Ultimate analysis of coal and their significance, calorific value Computation based on ultimate analysis data, Carbonization, Manufacturing of coke and recovery of by products. Cracking of higher Hydrocarbons and mechanism of cracking, Knocking, relationship between knocking and structure of hydrocarbon, improvement of anti knocking characteristics of IC engine fuels, Diesel engine fuels, Cetane number, combustion and it related numerical problems.

### Unit III

#### A. LUBRICANTS

Introduction, Mechanism of lubrication, Classification of lubricants, Properties and Testing- of lubricating oils, Numerical problems based on testing methods.

#### B. CEMENT AND REFRACTORIES

Manufacture, IS-code, Setting and hardening of cement, Refractory Introduction, classification and properties of refractories.

### Unit IV

#### HIGH-POL YMER

Introduction, types and classification of polymerization, Reaction Mechanism, Natural and Synthetic Rubber; Vulcanization of Rubber, Preparation, Properties and uses of the following-Polythene, PVC, PMA, PMMA, Teflon, Poly acrylonitrile, PVA, Nylon, Nylon 6:6, Terylene, Phenol formaldehyde, Urea Formaldehyde Resin, Glyptal, Silicone Resin, Polyurethanes; Butyl Rubber, Neoprene, Buna N, Buna S. Flow sheet manufacturing diagram of Nylon 6:6 and Decoran.



## **Unit V**

### **A. INSTRUMENTAL TECHNIQUES IN CHEMICAL ANALYSIS :**

Introduction, Principle, Instrumentation and applications of IR, NMR, UV, Visible, Gas Chromatography, Lambert's and Beer's Law

### **B. WATER ANALYSIS TECHNIQUES**

Alkalinity, hardness (Complexo-metric), Chloride, Free chlorine, DO, BOD and COD, Numerical problems based on above techniques.

## **ENGINEERING CHEMISTRY PRACTICAL**

*Note : At least 10 of the following core experiments must be performed during the session.*

### **1. Water Testing**

- (i) Determination of Total hardness by Complexometric titration method.
- (ii) Determination of mixed alkalinity
  - (a)  $\text{OH}^-$  and  $\text{CO}_3^{--}$
  - (b)  $\text{CO}_3^{--}$  and  $\text{HCO}_3^-$
- (iii) Chloride ion estimation by Argentometric method.

### **2. Fuels and lubricant testing :**

- (i) Flash and fire points determination by
  - (a) Pensky Martin Apparatus,
  - (b) Abel's Apparatus,
  - (c) Cleveland's open cup Apparatus.
  - (d) Calorific value by bomb calorimeter
- (ii) Viscosity and Viscosity index determination by
  - (a) Redwood viscometer No. 1
  - (b) Redwood viscometer No. 2
- (iii) Proximate analysis of coal
  - (a) Moisture content
  - (b) Ash content
  - (c) Volatile matter content
  - (d) Carbon residue
- (iv) Steam emulsification No. and Aniline point determination
- (v) Cloud and Pour point determination of lubricating oil.

### **3. Alloy Analysis**

- (i) Determination of percentage of Fe in an iron alloy by redox titration using N-Phenyl anthranilic acid as internal indicator.
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## Water and Its Treatment

*"As fire when thrown into water is cooled down and put out, so also a false accusation when brought against a man of the purest and holiest character boils over and is at once dissipated and vanishes"*

### 1 INTRODUCTION

For the existence of all living beings (humans, animals or plants) water is very crucial. Without water we cannot survive. Almost all human activities—domestic, agricultural and industrial demand use of water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources are available for ready use. Hence, it is urgently required to use the available water most carefully and economically. This chapter deals in Hardness and its estimation by EDTA method, alkalinity, water softening by zeolite and ion-exchange processes, domestic water treatment and desalination.

### 2 SPECIFICATIONS OF WATER FOR DIFFERENT USES

Different uses of water demand different specifications.

Few examples are discussed below :

(i) *Textile industry* needs frequent dyeing of clothes, and the water used by this industry should be soft and free from organic matter. If hard water is used, uniform dyeing is not possible. Because hard water decreases the solubility of acidic dyes. Basic dyes even precipitate out in such hard water. Organic matter imparts foul smell.

If the water contains Fe, Mn, colour or turbidity, it causes uneven dyeing and leaves stains on fabrics. Hence, water should be free from these impurities.

(ii) *Laundries* require soft water, free from colour, Mn and Fe. Because hardness increases consumption of soaps. Salts of Fe and Mn impart a grey or yellow shade to the fabric.

(iii) *Boilers* require water of zero hardness otherwise efficient heat transfer is prevented by scale formation. Untreated water can also lead to corrosion of boiler material, sometimes even explosion can also occur.

(iv) *Paper industry* requires water free from  $\text{SiO}_2$  (as it produces cracks in the paper) ; Turbidity, (Fe and Mn as they affect the brightness and colour of the paper) ; alkalinity (consumes alum and increases the cost of production) ; hardness (as Ca and Mg salts increase the ash content of the paper).

(v) *Bevarages* require water which should not be alkaline, as it destroys or modifies the taste as it tends to neutralize the fruit acids.

(vi) *Sugar industry* : If hard water (containing sulphates, nitrates etc.) is used in sugar refining it results in the formation of deliquescent sugar. Moreover, these impurities cause difficulty in the crystallization of sugar.



(vii) **Cooking** : water used for cooking should be free from dissolved salts producing hardness. Fuel requirement is high if hard water is used. Moreover, more time is required for cooking. Also if hard water is used for making tea or coffee, it imparts unpleasant taste and muddy-looking extract.

(viii) **Dairies and Pharmaceutical industries** require ultra pure water which should be colourless, tasteless, odourless and free from pathogenic organisms.

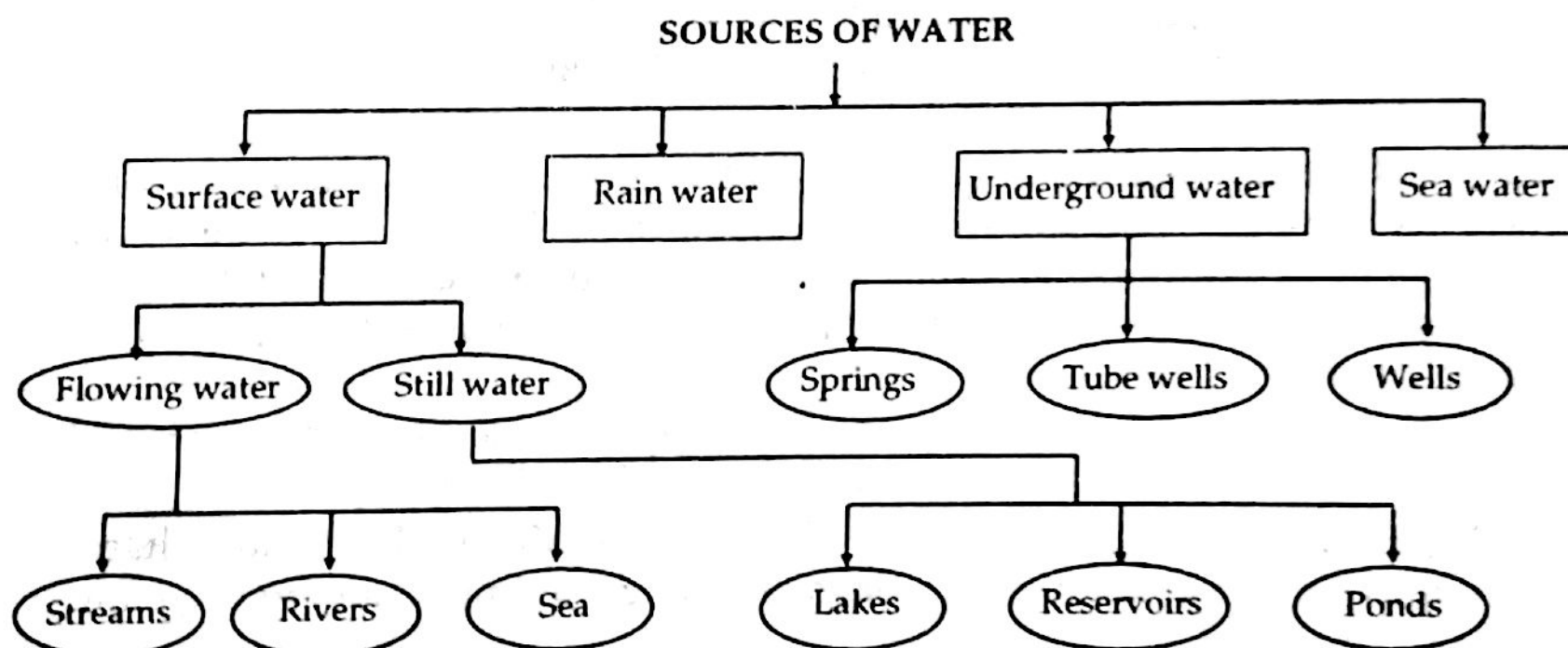
From the specifications of water for different industries, it can be concluded that water needs to be treated to remove all the undesirable impurities. "**Water treatment**" is the process by which all types of undesirable impurities are removed from water and making it fit for domestic or industrial purposes.

An effective water treatment requires a prior knowledge of nature and extent of impurities present in it.

### 3 SOURCES OF WATER

The main sources of water are :

- (i) **Surface water** : It includes flowing water (streams and rivers) and still water (lakes, ponds and reservoirs).
- (ii) **Underground water** : It includes water from wells and springs.
- (iii) **Rain water** and
- (iv) **Sea water**.



**River water** contains dissolved minerals like chlorides, sulphates, bicarbonates of sodium, magnesium, calcium and iron. It also contains suspended impurities of sand and rock and organic matter. The composition of river water is not constant. The amount of dissolved impurities in it depends on its contact of the soil. Greater the duration of contact, more soluble are the minerals of soil in it.

**Lake water** has high quantity of organic matter present in it but lesser amounts of dissolved minerals. Its chemical composition is also constant.

**Rain water** is obtained as a result of evaporation from the surface water. Probably it is the purest form of natural water. But during its downward journey through the atmosphere it dissolves organic and inorganic suspended particles and considerable amount of industrial gases like ( $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_2$  etc.). Rain water is expensive to collect and is irregular in supply.



*Underground water* is free from organic impurities and is clearer in appearance due to the filtering action of the soil. But it contains large amount of dissolved salts.

*Sea water* is very impure due to two reasons : continuous evaporation increases the dissolved impurity content which is further increased by the impurity thrown by rivers as they join sea. It is too saline for most industrial uses except cooling.

#### 4 IMPURITIES IN WATER

The following types of impurities are present in water :

(i) *Suspended impurities* : These impurities impart turbidity, colour and odour to water. It may be inorganic (clay and sand) or organic (oil globules, vegetable and animal matter) in nature.

(ii) *Colloidal impurities* : Products from organic waste, finely divided silica and clay etc., are agents which come under colloidal impurities.

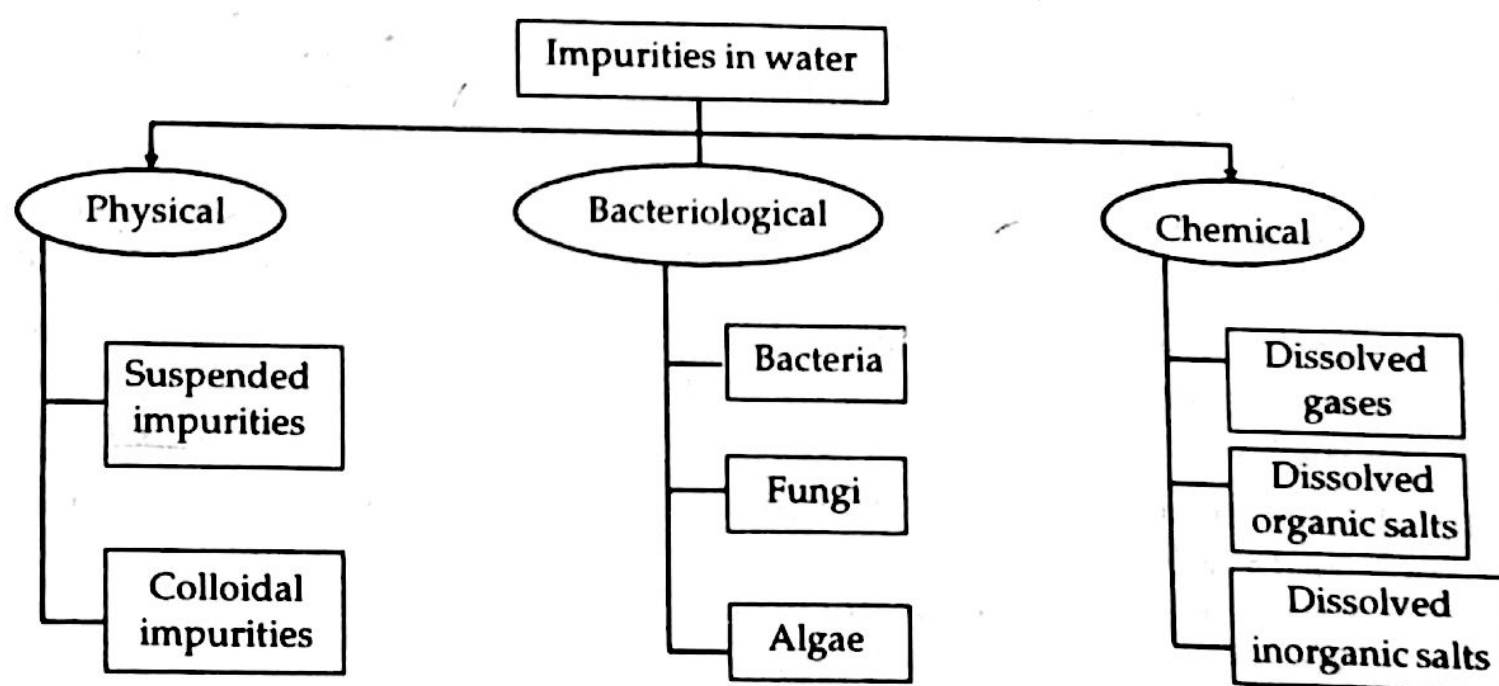
(iii) *Dissolved impurities* : It may be due to the presence of dissolved salts like carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron and sodium. Hardness in water is due to the presence of these salts.

Dissolved gases like  $O_2$ ,  $CO_2$ , etc., also come under this category.

(iv) *Microorganisms* : They include bacterias, fungi and algae.

These bacteriological impurities make water dangerous for human consumption. These disease producing pathogenic micro-organisms are introduced into water by animal or vegetable waste and through sewage flowing into the river.

To sum up, impurities in water are of following types :



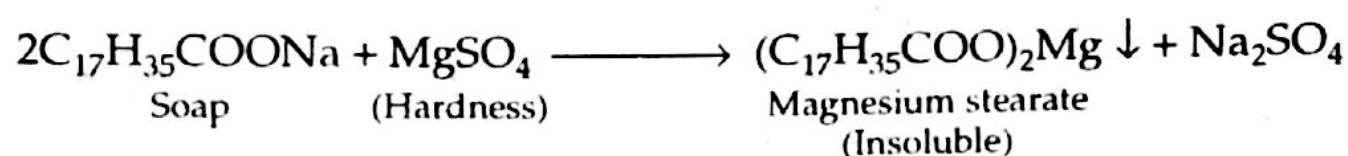
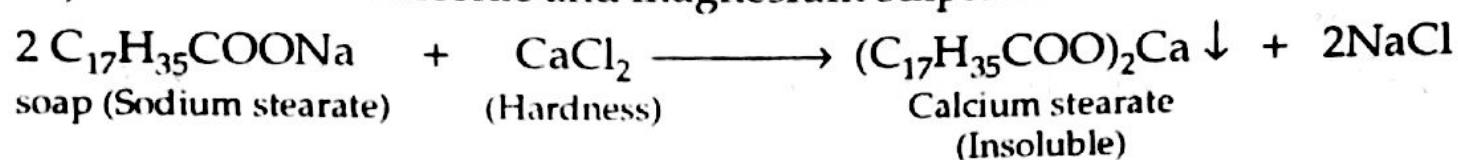
#### Sources of Impurities in Water

Following are the sources of impurities in water :

- Gases (e.g.,  $O_2$ ,  $CO_2$ , etc.,) are picked up from the atmosphere by rain water.
- Decomposition of plant and animal remains introduce organic impurities in water.
- Water takes impurities when it comes in contact with ground, soil or rocks.
- Impurities are also introduced in water when it comes in contact with sewage or industrial waste.

## 5 HARDNESS OF WATER

**Hardness** in water is that characteristic, "which prevents the lathering of soap". Originally, it was defined as the soap consuming capacity of water sample. This is due to presence in water of certain salts of Ca, Mg and other heavy metal ions like  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  dissolved in it. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms insoluble white scum or precipitate which do not possess any detergent action. This is due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are shown below :



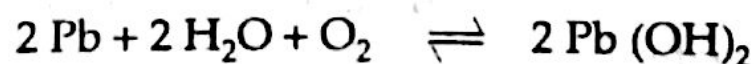
In fact, any cation which produces insoluble soap with soap solution will contribute to hardness. Thus, on this basis water can be classified into two types : viz., Hard and Soft water. The essential differences between the two are summarized in Table 1 :

Table 1

S. No.	Hard Water	Soft Water
1.	Water which does not produce lather with soap solution readily, but forms a white curd, is called "hard water".	Water which lathers easily on shaking with soap solution, is called "soft water".
2.	Hard water contains dissolved Calcium and Magnesium salts in it.	Soft water does not contain dissolved calcium and magnesium salts in it.
3.	In hard water, cleansing quality of soap is depressed and a lot of it is wasted during Washing and Bathing.	In soft water, cleansing quality of soap is not depressed and so soap is not wasted during washing and bathing.
4.	Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking.	Less fuel and time are required for cooking in soft water.

**Q. Why water should not be soft for drinking purposes ?**

**Ans.** Since soft water is plumbo-solvent (it attacks lead used in plumbing),  
via.



The solubility of Pb in water is diminished in the presence of  $\text{HCO}_3^-$  ions.

**Note.** A partial softening leaving a residual total-hardness of about 85 ppm  $\text{CaCO}_3$  equivalents is generally adopted for drinking purposes.



It is of following types :

Thus, the salts responsible for temporary hardness are  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ .

$$\text{Ca(HCO}_3\text{)}_2 \xrightarrow{\text{boil}} \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$$

Calcium bicarbonate                      Calcium carbonate  
(insoluble)

Advantages and disadvantages of hard water are summarized in Table 2 below :

Table 2

S. No.	Hard Water	
	Advantages	Disadvantages
1.	The taste of hard water is usually better than soft water. The label on the bottle of mineral water shows that it contains $Mg^{2+}$ and $Ca^{2+}$ ions and it tastes good.	Hard water produces scum with soap. Thus, the washed clothes look dull. Efficiency of soap decreases in hard water so economy decreases.
2.	The dissolved calcium in hard water can help to produce strong teeth and healthy bones in children.	Boiler feed water should be free from hardness otherwise even explosion can occur.
3.	In old houses, lead piping was used for distribution of water. Hard water coats these with a layer of insoluble $CaCO_3$ . This prevents any of the poisonous lead dissolving in the drinking water.	

### Indications of Hard Water

Hard water interferes with almost every cleaning task, from laundering and dishwashing to bathing and personal grooming. Few specific situations are summarized below, which indicate that use water is hard :

- (i) Clothes laundered in hard water may look dull and feel harsh and scratchy,
- (ii) Dishes and glasses may be spotted when dry,
- (iii) Hard water may cause a film on glass shower doors, shower walls, bath tubs, sinks, etc.
- (iv) Hair washed in hard water may feel sticky and look dull.
- (v) Water flow may be reduced by hard water deposits in pipes.
- (vi) Heated hard water forms a scale which subsequently contribute to the inefficient operation or failure of water-using appliances.

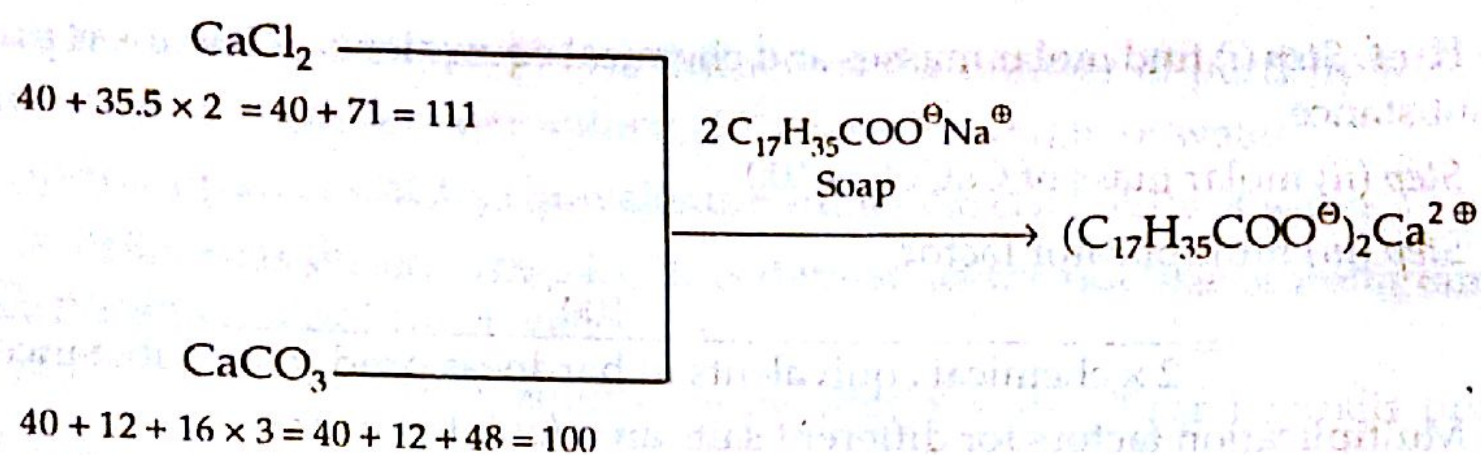
### Degree of Hardness

Although hardness of water is never present in the form of calcium carbonate because it is insoluble in water, hardness of water is conveniently expressed in terms of equivalent amount (*equivalents*) of  $CaCO_3$ .

The reason for choosing  $CaCO_3$  as the standard for reporting hardness of water is the ease in calculations as its molecular weight is exactly 100. Moreover, it is the most insoluble salt that can be precipitated in water treatment.

Suppose a given water is hard due to the presence of  $CaCl_2$ . The soap consuming capacity of this hard water and a standard hard water containing  $CaCO_3$  can be calculated by using following equation :





Thus, 111 parts by weight of  $\text{CaCl}_2$  would react with the same amount of soap as 100 parts by weight of  $\text{CaCO}_3$ .

Thus, in order to convert the amount of  $\text{CaCl}_2$  present (Let  $w$  milli grams per litre) as its  $\text{CaCO}_3$  equivalent, the amount of  $\text{CaCl}_2$  should be multiplied by a factor of  $100/111$ .

$$\begin{aligned}
 &1 \text{ gram mole of } \text{CaCl}_2 \equiv 1 \text{ gram mole of } \text{CaCO}_3 \\
 \Rightarrow &111 \text{ gram of } \text{CaCl}_2 \equiv 100 \text{ gram of } \text{CaCO}_3 \\
 \Rightarrow &1 \text{ gram of } \text{CaCl}_2 \equiv \frac{100}{111} \text{ gram of } \text{CaCO}_3 \\
 \Rightarrow &w \text{ (mg/L) of } \text{CaCl}_2 \equiv \frac{100}{111} \times w \text{ (mg/L) of } \text{CaCO}_3 \\
 &= \frac{50}{55.5} \times w \text{ (mg/L) of } \text{CaCO}_3
 \end{aligned}$$

$$\therefore \text{Equivalent of } \text{CaCO}_3 \text{ for a hardness causing substance } \text{CaCl}_2 = \frac{\text{Equivalent weight of } \text{CaCO}_3}{\text{Equivalent weight of } \text{CaCl}_2} \times w \text{ (mg/L)}$$

In general,

$$\text{Equivalents of } \text{CaCO}_3 = \frac{\left[ \begin{array}{c} \text{Strength of hardness} \\ \text{producing substance} \\ \text{(in mg/L)} \end{array} \right] \times \left[ \begin{array}{c} \text{Chemical equivalent} \\ \text{of } \text{CaCO}_3 \\ \text{(= 50)} \end{array} \right] \times 2}{\left[ \text{Chemical equivalent of hardness Producing substance} \right] \times 2}$$

$$\begin{aligned}
 &= \left[ \begin{array}{c} \text{Strength of hardness} \\ \text{producing substance} \\ \text{in mg/L} \end{array} \right] \times \left[ \frac{100}{2 \times \text{Chemical equivalents of hardness producing substance}} \right] \\
 &= \left[ \begin{array}{c} \text{Strength of hardness} \\ \text{producing substance} \\ \text{in mg/L} \end{array} \right] \times (\text{Multiplication factor}) \text{ in } \frac{\text{mg}}{\text{L}} \text{ or ppm}
 \end{aligned}$$

**Example 1.** Given atomic weights of elements as  $\text{H} = 1$ ,  $\text{C} = 12$ ,  $\text{N} = 14$ ,  $\text{O} = 16$ ,  $\text{Na} = 23$ ,  $\text{Mg} = 24$ ,  $\text{Al} = 27$ ,  $\text{S} = 32$ ,  $\text{Cl} = 35.5$ ,  $\text{Ca} = 40$ ,  $\text{Fe} = 56$ .

Find multiplication factor for converting into equivalents of  $\text{CaCO}_3$ .

For  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CO}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{HCO}_3^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NaAlO}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}^+$



**Hint.** Step (i) find molar masses and chemical equivalents of hardness producing substance

Step (ii) molar mass of  $\text{CaCO}_3$  is 100

Step (iii) multiplier factor

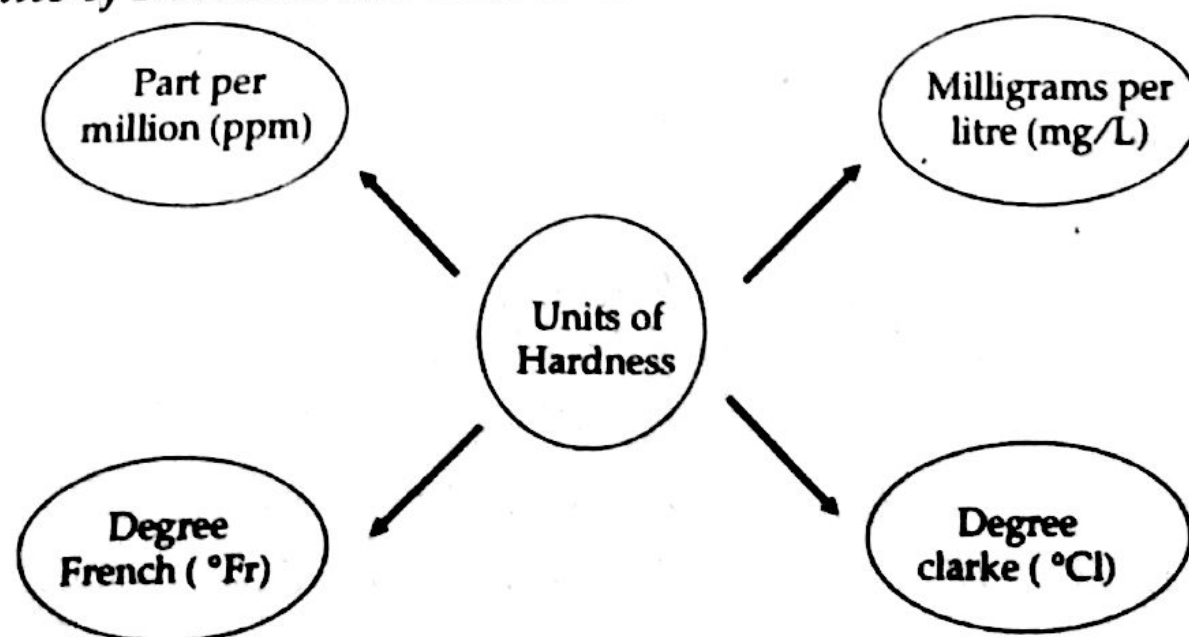
$$= \frac{100}{2 \times \text{chemical equivalents of hardness producing substance}}$$

Multiplication factors for different salts are tabulated in Table 3.

**Table 3**

Constituent salt/ion	Molar mass	n-factor	Chemical equivalent $= \frac{\text{Molar mass}}{\text{n-factor}}$	Multiplication factor for converting into equivalents of $\text{CaCO}_3$
$\text{Ca}(\text{HCO}_3)_2$	162	2	$162/2 = 81$	$100/(2 \times 81) = 100/162$
$\text{Mg}(\text{HCO}_3)_2$	146	2	$146/2 = 73$	$100/(2 \times 73) = 100/146$
$\text{CaSO}_4$	136	2	$136/2 = 68$	$100/(2 \times 68) = 100/136$
$\text{MgSO}_4$	120	2	$120/2 = 60$	$100/(2 \times 60) = 100/120$
$\text{CaCl}_2$	111	2	$111/2 = 55.5$	$100/(2 \times 55.5) = 100/111$
$\text{MgCl}_2$	95	2	$95/2 = 47.5$	$100/(2 \times 47.5) = 100/95$
$\text{CaCO}_3$	100	2	$100/2 = 50$	$100/(2 \times 50) = 100/100$
$\text{MgCO}_3$	84	2	$84/2 = 42$	$100/(2 \times 42) = 100/84$
$\text{CO}_2$	44	2	$44/2 = 22$	$100/(2 \times 22) = 100/44$
$\text{Mg}(\text{NO}_3)_2$	148	2	$148/2 = 74$	$100/(2 \times 74) = 100/148$
$\text{HCO}_3^-$	61	1	$61/1 = 61$	$100/(2 \times 61) = 100/122$
$\text{OH}^-$	17	1	$17/1 = 17$	$100/(2 \times 17) = 100/34$
$\text{CO}_3^{2-}$	60	2	$60/2 = 30$	$100/(2 \times 30) = 100/60$
$\text{NaAlO}_2$	82	1	$82/2 = 82$	$100/(2 \times 82) = 100/164$
$\text{Al}_2(\text{SO}_4)_3$	342	6	$342/6 = 57$	$100/(2 \times 57) = 100/114$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	2	$278/2 = 139$	$100/(2 \times 139) = 100/278$
$\text{H}^+$	1	1	$1/1 = 1$	$100/(2 \times 1) = 100/2$

**Units of Hardness and their inter-relations :**



(i) *Parts per million (ppm)* : It is defined as the number of parts by weight of calcium carbonate present per million ( $10^6$ ) parts by weight of water, i.e., 1 ppm = 1 part of  $\text{CaCO}_3$  equivalents hardness in ( $10^6$ ) parts of water.

(ii) *Milligrams per litre (mg/L)* : It is defined as the number of milligrams of  $\text{CaCO}_3$  present in one litre of water, i.e., 1 mg/L = 1 mg of  $\text{CaCO}_3$  equivalent per liter of water. It can be easily proved that 1 mg/L = 1 ppm for water

As for water, 1 L = 1 kg =  $10^6$  mg

$\therefore$  1 mg of  $\text{CaCO}_3$  eq-hardness per L of water

= 1 mg of  $\text{CaCO}_3$  eq-hardness per  $10^6$  mg of water

= 1 part of  $\text{CaCO}_3$  per  $10^6$  parts of water = 1 ppm

Hence, 1 mg/L = 1 ppm

(iii) *Degree clarke ( $^{\circ}\text{Cl}$ )* : It is defined as the parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

Or It is number of grains of  $\text{CaCO}_3$  equivalent hardness per gallon of water.

i.e., 1  $^{\circ}\text{Cl}$  = 1 part of  $\text{CaCO}_3$  per 70,000 parts of water.

(iv) *Degree French ( $^{\circ}\text{Fr}$ )* : It is defined as the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

i.e., 1  $^{\circ}\text{Fr}$  = 1 part of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

*Relationships between various units of hardness :*

As. 1 ppm = 1 part per  $10^6$  parts of water

1  $^{\circ}\text{Fr}$  = 1 part per  $10^5$  part of water

and 1  $^{\circ}\text{Cl}$  = 1 part per 70,000 parts of water

$\therefore$   $10^6$  ppm =  $10^5$   $^{\circ}\text{Fr}$  = 70,000  $^{\circ}\text{Cl}$

Hence, 1 ppm = 0.1  $^{\circ}\text{Fr}$  = 0.07  $^{\circ}\text{Cl}$  = 1 mg/L.

$\downarrow \rightarrow$	ppm	mg/l	$^{\circ}\text{Fr}$	$^{\circ}\text{Cl}$
ppm	1	1	0.1	0.07
mg/l	1	1	0.1	0.07
$^{\circ}\text{Fr}$	10	10	1	0.7
$^{\circ}\text{Cl}$	1/0.07	1/0.07	1/0.7	1

Table 1 adapted from the Water Quality Association (WQA), shows hardness classifications

**Table 1. Classification of Water Hardness.**

Classification	Soft	Slightly hard	Moderately hard	Hard	Very hard
ppm or mg/L	0 – 17	17 – 60	60 – 120	120 – 180	180 and above

### 5.1 Solved Examples based on Determination of Hardness of Water

**Example 1.** A water sample contains 410 mg of  $\text{CaSO}_4$  per litre. Calculate the hardness in terms of  $\text{CaCO}_3$  equivalents. [RGPV, Dec. 2001]

**Solution.** Hardness = (strength of  $\text{CaSO}_4$  in mg/L)  $\times$  multiplication factor

$$\begin{aligned}
 &= (\text{strength of } \text{CaSO}_4 \text{ in mg/L}) \times \left[ \frac{\text{chemical equivalents of } \text{CaCO}_3}{\text{chemical equivalents of } \text{CaSO}_4} \right] \\
 &= (410 \text{ mg/L}) \times \left[ \frac{50}{68} \right] \\
 &= 301.47 \text{ mg/L} = 301.47 \text{ ppm}
 \end{aligned}$$

**Example 2.** How many grams of  $\text{MgCO}_3$  dissolved per litre gives 84 ppm of hardness?

**Solution.** Hardness

$$= (\text{strength of } \text{MgCO}_3 \text{ in mg/L}) \times \left[ \frac{\text{chemical equivalent of } \text{CaCO}_3}{\text{chemical equivalent of } \text{MgCO}_3} \right]$$

Hence, strength of  $\text{MgCO}_3$  = Hardness  $\times \frac{\text{chemical equivalents of } \text{MgCO}_3}{\text{chemical equivalents of } \text{CaCO}_3}$

$$= (84 \text{ ppm}) \times \left( \frac{42}{50} \right) = 70.56 \text{ ppm} = 70.56 \text{ mg/L}$$

Thus,  $70.56 \times 10^{-3}$  gms of  $\text{MgCO}_3$  dissolved per litre gives 84 ppm of hardness.

**Example 3.** A sample of water on analysis was found to contain the following impurities :

Impurity	$\text{Ca}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2$	$\text{CaSO}_4$	$\text{MgSO}_4$
Quantity (mg/L)	4	6	8	10
Mol. Wt.	162	146	136	120

Calculate the temporary, permanent and total hardness of water in ppm,  $^\circ\text{Fr}$  and  $^\circ\text{Cl}$ .

**Solution.** Step (i) Conversion into  $\text{CaCO}_3$  equivalents :

Constituent	Amount mg/L [A]	Multiplication factor [M]	$\text{CaCO}_3$ equivalent = [A] $\times$ [M]
$\text{Ca}(\text{HCO}_3)_2$	4	100/162	$4 \times \frac{100}{162} = 2.47 \text{ mg/L}$
$\text{Mg}(\text{HCO}_3)_2$	6	100/146	$6 \times \frac{100}{146} = 4.11 \text{ mg/L}$
$\text{CaSO}_4$	8	100/136	$8 \times \frac{100}{136} = 5.88 \text{ mg/L}$
$\text{MgSO}_4$	10	100/120	$10 \times \frac{100}{120} = 8.33 \text{ mg/L}$



*Step (ii) Determination of Temporary Hardness :*

As Temporary hardness is due to bicarbonates of Calcium and Magnesium

$$\therefore \text{Temporary hardness} = 2.47 + 4.11 = 6.58 \text{ mg/L}$$

$$\text{As } 1 \text{ mg/L} = 1 \text{ ppm} = 0.1^\circ\text{Fr} = 0.07^\circ\text{Cl}$$

$$\text{Hence, Temporary hardness} = 6.58 \text{ mg/L} = 6.58 \text{ ppm}$$

$$= 6.58 \times 0.1 = 0.658^\circ\text{Fr}$$

$$= 6.58 \times 0.07 = 0.46^\circ\text{Cl}$$

*Step (iii) Determination of Permanent Hardness :*

As permanent hardness in this case is due to  $\text{CaSO}_4$  and  $\text{MgSO}_4$

$$\therefore \text{Permanent hardness} = 5.88 + 8.33 = 14.21 \text{ mg/L}$$

$$= 14.21 \text{ ppm}$$

$$= 14.21 \times 0.1 = 1.421^\circ\text{Fr}$$

$$= 14.21 \times 0.07 = 0.995^\circ\text{Cl}$$

**Example 4.** 200 mL of water sample has a hardness equivalent to 25 mL of 0.08 N  $\text{MgSO}_4$ . Find the hardness in  $^\circ\text{Fr}$ .

**Solution.** As Normality is number of gm. equivalents per L of solution.

Hence, number of gm. equivalents of  $\text{MgSO}_4$

$$= \text{volume of } \text{MgSO}_4 \times \text{its normality}$$

$$= \frac{25}{1000} \times 0.08 = 2 \times 10^{-3}$$

$$\text{As Number of gm. equivalents} = \frac{\text{Weight in gms.}}{\text{Eq. wt.}}$$

Thus weight in gms. of  $\text{MgSO}_4$ , present in 200 mL of water sample

$$= (2 \times 10^{-3}) \times \text{Eq. wt. of } \text{MgSO}_4$$

So, wt. in gms. of  $\text{MgSO}_4$  per L of water

$$= (2 \times 10^{-3}) \times \text{Eq. wt. of } \text{MgSO}_4 \times \frac{1000}{200} = 10^{-2} \times \text{Eq. wt.}$$

$$\text{Now Hardness} = (\text{Wt. in gms. of } \text{MgSO}_4 \text{ per L of water}) \times \frac{50}{\text{Eq. wt. of } \text{MgSO}_4}$$

$$= (10^{-2} \times \text{Eq. wt. of } \text{MgSO}_4) \times \frac{50}{\text{Eq. wt. of } \text{MgSO}_4}$$

$$= 50 \times 10^{-2} \text{ gm/L} = 500 \text{ mg/L}$$

$$= 500 \text{ ppm}$$

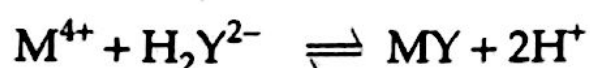
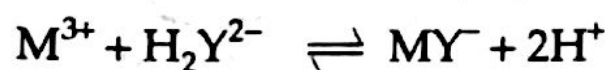
$$= 500 \times 0.1 = 50^\circ\text{Fr} \quad (\text{Since } 1 \text{ ppm} = 0.1^\circ\text{Fr})$$

## 6 ESTIMATION OF WATER HARDNESS BY EDTA METHOD

Water hardness is generally caused by the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions present in water. Some other polyvalent ions like strontium, iron, aluminium, zinc and manganese etc., also contribute to hardness. But because of their very low concentration in natural water, hardness is generally measured as concentration of only calcium and magnesium ions.

The analysis is done by complexometric titration using standard EDTA as titrant and EBT as an indicator.

Ethylene diamminetetra acetic acid (EDTA) is tetraprotic acid. (Let it is represented by the symbol  $H_4 Y$ ). Because of its limited solubility, it is *not used directly*. It is usually employed as the soluble disodium salt dihydrate  $Na_2H_2Y \cdot 2H_2O$  because it can be obtained in high state of purity (Molecular weight = 372.24) and is a primary standard. The solutions of EDTA are very valuable titrants because the reagent combines with metal ions in a 1 : 1 ratio. Irrespective of the charge on the cation, the resultant complexes have similar structures but differ from one another in the charge they carry. The reactions of cations with EDTA may be written as :



The equilibrium is markedly affected by the pH of the solution, viz, the complexes of EDTA with divalent metals are stable in basic or slightly acidic solutions.

The structures of the anion  $H_2Y^{2-}$  and its complex with divalent metal ion,  $M^{2+}$ , are shown in Fig. 1.

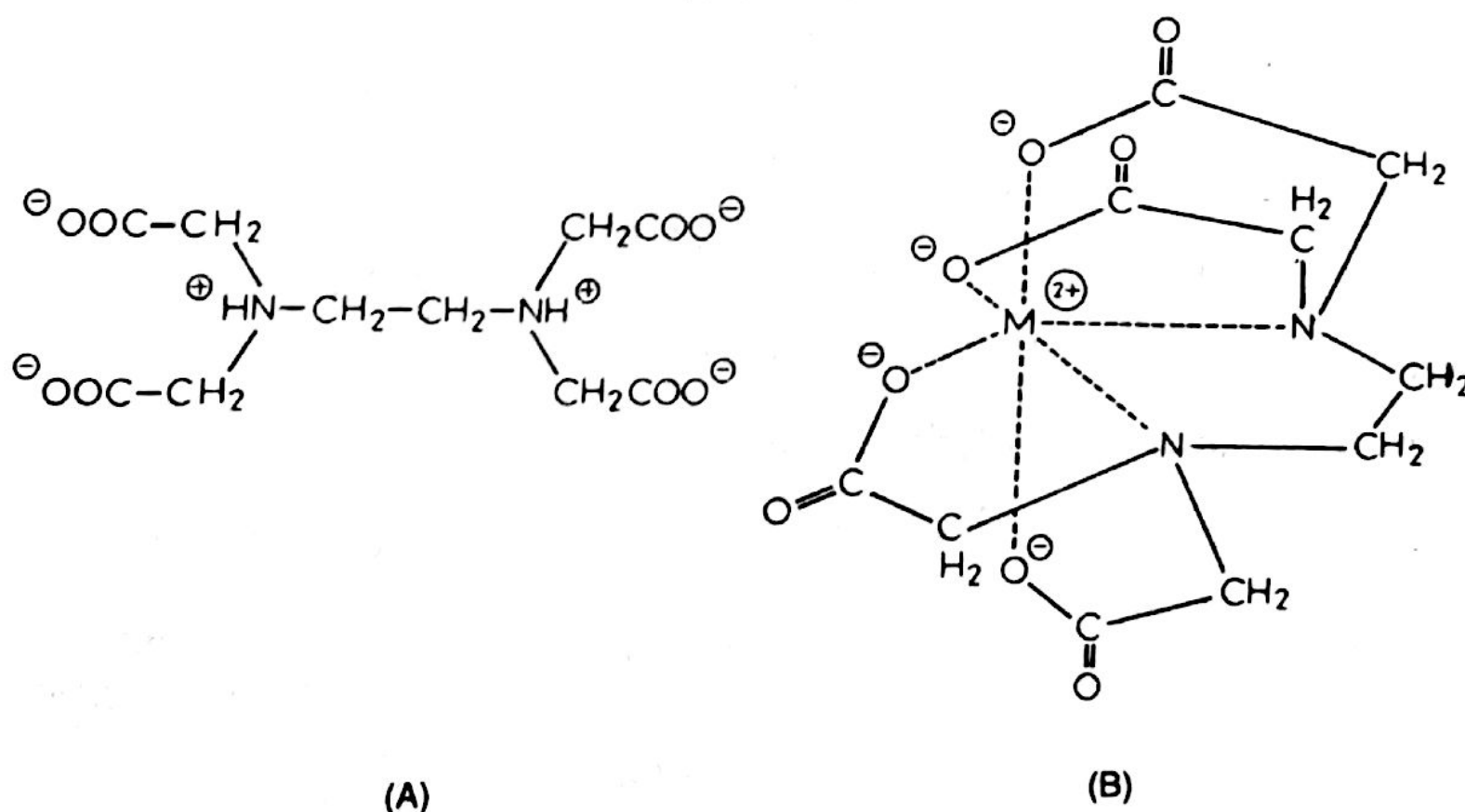


Fig. 1. Structures of ethylene diamminetetraacetic acid (EDTA) and metal-EDTA chelates : (A) structure of the dianion of EDTA,  $H_2Y^{2-}$  ; (B) structure of an  $M^{2+}$  -EDTA chelate,  $MY^{2-}$ .

We can think of the EDTA anion as surrounding a metal ion like the large claw of a crab grasping its prey. The technical term for such a complex is *chelate*, which comes from the Greek word meaning a pincerlike claw.

The chelates formed by EDTA are sufficiently stable to form the basis for a titrimetric method. The great stability undoubtedly results from the several complexing sites within the molecule that give rise to a cage like structure in which the cation is effectively surrounded and isolated from solvent molecules.



**Eriochrome Black T (EBT)** : It is a typical metal-ion indicator, chemically it is sodium 1 - (1-hydroxy-2-naphthylazo) -6-nitro-2-naphthol-4-sulphonate. Its structure is shown in Fig. 2.

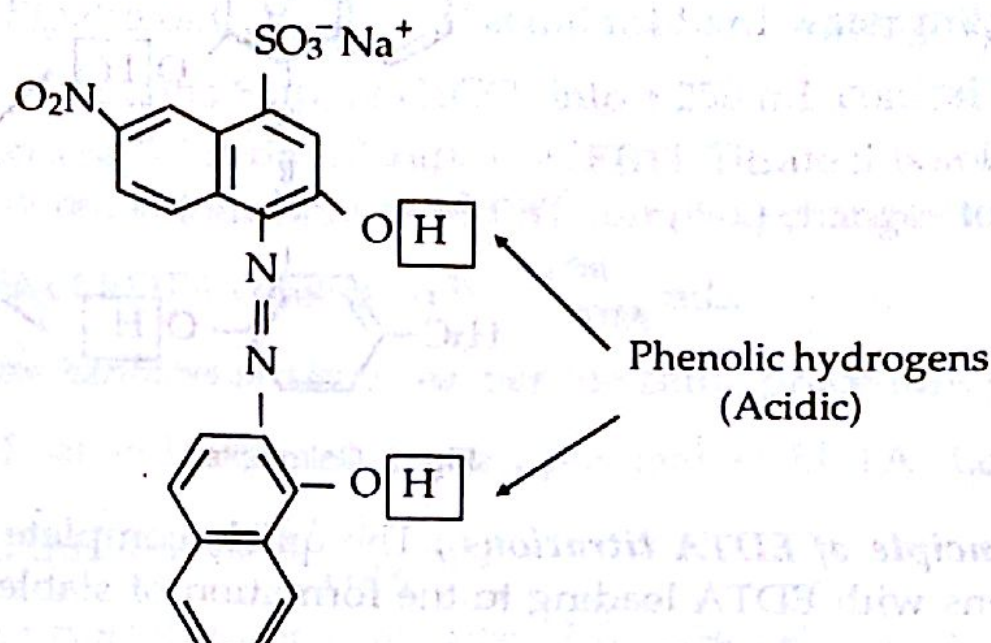
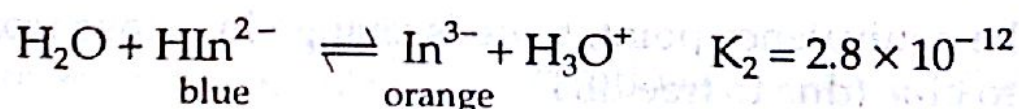
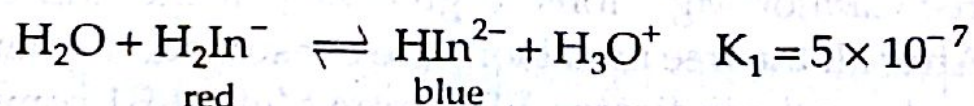
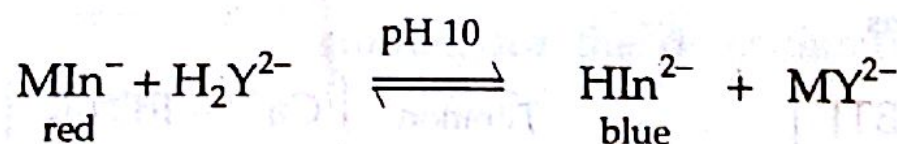


Fig. 2. Eriochrome Black T [ $\text{EBT} = \text{H}_2 \text{In}^-$ ].

It contains a sulfonic acid group, which is completely ionized in water and two phenolic groups that only partially ionize. Its behaviour as a weak acid is described by the equations :



The acids and their conjugate bases have different colours. EBT also forms complexes with metal ions which are generally wine-red, as is  $\text{H}_2\text{In}^-$ . Thus, EBT behaves as an acid/base indicator as well as metal-ion indicator. For metal ion detection, it is necessary to adjust the pH on the basic side so that the blue form of the species,  $\text{HIn}^{2-}$ , predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is wine-red. With the first slight excess of EDTA, the solution turns blue as a consequence of the reaction (buffered at pH 10) :



The EDTA displaces the indicator from the metal-indicator complex because the equilibrium-constant for the formation of the EDTA-metal ion complex is much larger than that for the indicator-metal ion complex, this produces a reasonably sharp colour change at the equivalence point.

A limitation of Eriochrome Black T is that its solutions are not stable. They decompose slowly on standing ; refrigeration slows this process. Another indicator, *calmagite* (structure shown in Fig. 3) does not suffer from this disadvantage. And for all practical purposes, its behaviour is identical to Eriochrome Black T.



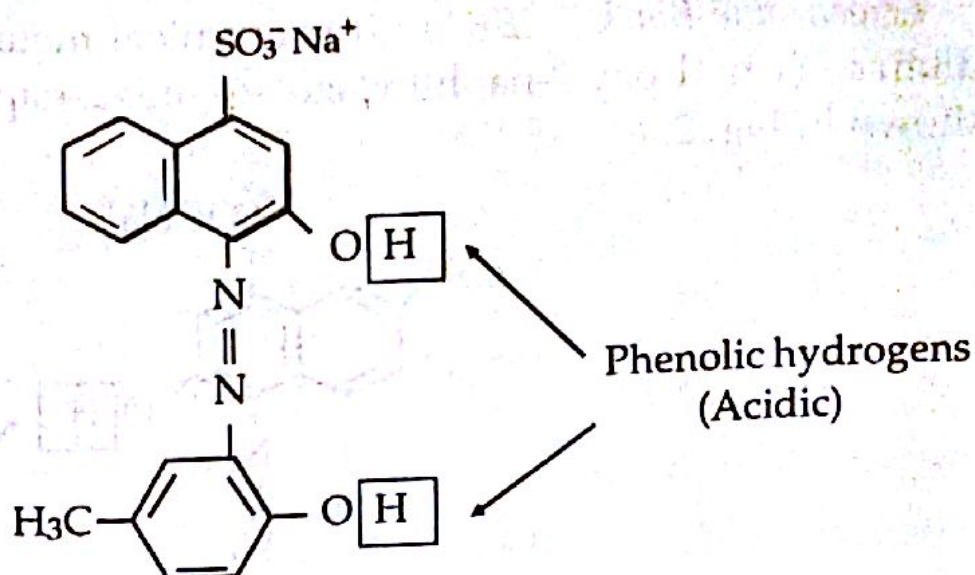


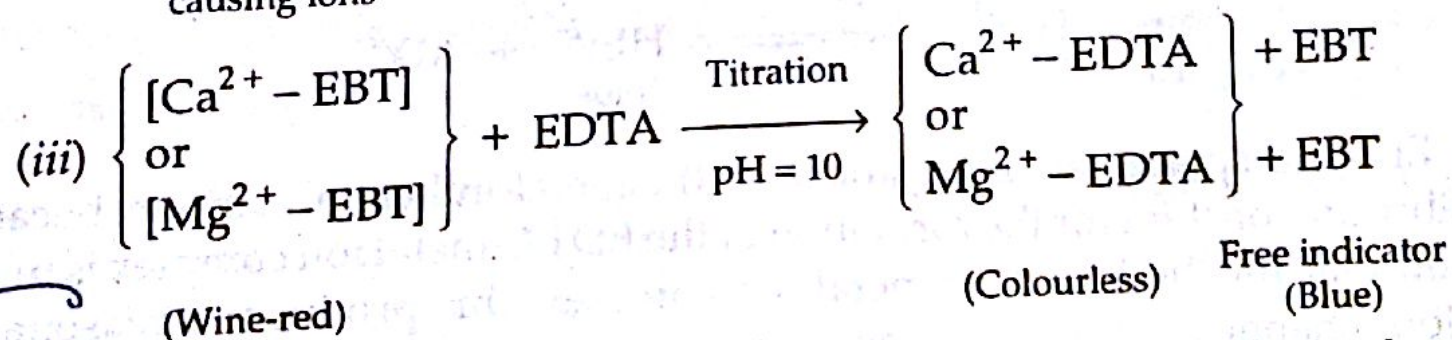
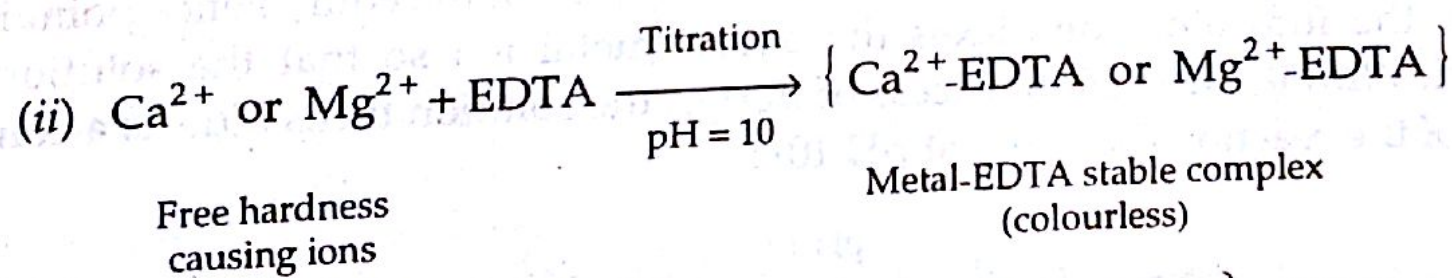
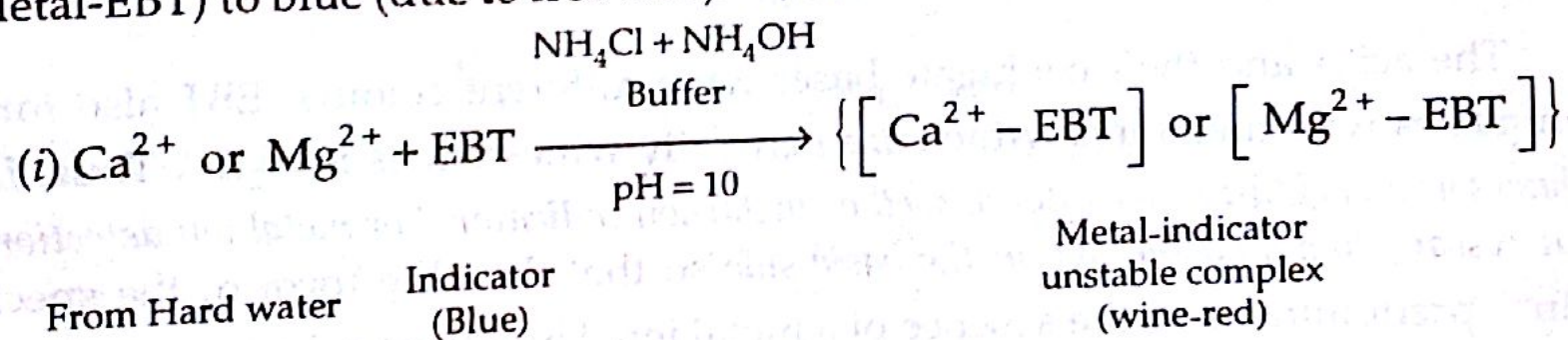
Fig. 3. Calmagite.

**Principle of EDTA titrations :** The quick, complete and 1 : 1 interaction of metal ions with EDTA leading to the formation of stable complex is the basis of complexometric titrations.

**Theory :** The hard water is buffered to a pH value of ~10 using  $\text{NH}_4\text{OH} - \text{NH}_4\text{Cl}$  buffer and a few drops of EBT indicator solution are added. EBT forms a weak complex with metal ions, which has a wine-red colour.

In the course of the titration of water sample against EDTA, EDTA first combines with free  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions to give very stable and colourless metal-EDTA complex. After all the free metal ions are consumed, the next drop of added EDTA solution displaces the indicator, EBT, from Metal-EBT complex.

Thus, at the equivalence point, there is change in colour from wine-red (due to Metal-EBT) to blue (due to free EBT).



The total hardness is thus determined. For the determination of permanent hardness, temporary hardness is first removed by boiling. After the removal of precipitate by filtration, the permanent hardness in the filtrate is determined by titration with EDTA as before. Temporary hardness is then determined by subtracting permanent hardness from total hardness.



**Procedure :**

(i) *Standardization of EDTA solution.* Fill up the burette with EDTA solution after washing and rinsing. Pipette out,  $V_{SHW}^{Std}$  of standard hard water prepared in such a way that 1 mL of it contains  $S$  mg of  $CaCO_3$  into a 250 mL conical flask. Add 10 mL of buffer solution and 2-3 drops of indicator (EBT). Titrate this solution against EDTA until the wine-red colour (due to M-EBT complex) changes to blue (due to EBT). Let the volume of EDTA consumed be  $V_{EDTA}^{Std}$  mL.

(ii) *Determination of total hardness of water.* As per the same procedure given above, titrate  $V_{UHW}^{TH}$  mL of unknown water sample against EDTA. Let the volume of EDTA consumed this time be  $V_{EDTA}^{TH}$  mL.

(iii) *Determination of permanent hardness of water.* Take 250 mL of the water sample in a 500 mL beaker and boil it till the volume is reduced to about 50 mL. This step causes all the bicarbonates to decompose respectively into insoluble  $CaCO_3$  and  $Mg(OH)_2$ . Filter and wash the precipitate with distilled water and quantitatively collect the filtrate and washings in a 250 mL conical flask and make up the volume to 250 mL with distilled water. Titrate  $V_{UHW}^{PH}$  mL of this water sample against EDTA as in step (i). Let the volume of EDTA used be  $V_{EDTA}^{PH}$ .

**Observations :**

$S =$	Strength in grams per litre of standard hard water (SHW),
$V_{SHW}^{Std} =$	Volume of standard hard water (SHW) used for standardization (Std),
$V_{EDTA}^{Std} =$	Volume of EDTA consumed for standardization (Std) titration,
$V_{UHW}^{TH} =$	Volume of unknown hard water (UHW) used for the determination of total hardness (TH),
$V_{EDTA}^{TH} =$	Volume of EDTA consumed for the determination of total hardness (TH),
$V_{UHW}^{PH} =$	Volume of unknown hard water (UHW) used for the determination of permanent hardness (PH),
$V_{EDTA}^{PH} =$	Volume of EDTA consumed for the determination of permanent hardness (PH).

**Calculations :****Approach I : Based on Unitary Method****Step (i) : Standardization of EDTA solution :**

Given, one mL of standard hard water (SHW) contains  $S$  mg of  $CaCO_3$  equivalent hardness.

$$\therefore 1 \text{ mL of SHW} = S \text{ mg } CaCO_3$$

$$\Rightarrow V_{SHW}^{Std} \text{ mL of SHW} = \left( S \times V_{SHW}^{Std} \right) \text{ mg } CaCO_3$$



Now,  $V_{\text{EDTA}}^{\text{Std}}$  mL of EDTA =  $V_{\text{SHW}}^{\text{Std}}$  mL of SHW

$$= \left( S \times V_{\text{SHW}}^{\text{Std}} \right) \text{mg CaCO}_3$$

$$\Rightarrow 1 \text{ mL of EDTA} = \left( \frac{S \times V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right) \text{mg CaCO}_3 \quad \dots(1)$$

**Step (ii) : Determination of Total hardness (TH) of unknown hard water (UHW) :**

$$V_{\text{UHW}}^{\text{TH}} \text{ mL of UHW} = V_{\text{EDTA}}^{\text{TH}} \text{ mL of EDTA}$$

Using equation (i), right hand side of above equation becomes

$$V_{\text{UHW}}^{\text{TH}} \text{ mL of UHW} = V_{\text{EDTA}}^{\text{TH}} \times \left( \frac{S \times V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right) \text{mg CaCO}_3$$

$$\Rightarrow 1 \text{ mL of UHW} = \left( \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} \times S \times \frac{V_{\text{EDTA}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right) \text{mg CaCO}_3$$

$$\Rightarrow 1,000 \text{ mL of UHW} = \left[ 1000 \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} \times S \times \frac{V_{\text{EDTA}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right] \text{mg CaCO}_3$$

$$\therefore \boxed{\text{Total hardness} = \left[ 1000 \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{SHW}}^{\text{TH}}} \times S \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right] \text{mg/L}} \quad \dots(2)$$

**Step (iii) : Determination of permanent hardness (PH) of unknown hard water (UHW) :**

$$V_{\text{UHW}}^{\text{PH}} \text{ mL of boiled water} = V_{\text{EDTA}}^{\text{PH}} \text{ mL of EDTA}$$

Calculation steps, similar to as is done in step (ii) above, will give us,

$$1,000 \text{ mL of boiled water} = \left[ 1,000 \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \times S \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right] \text{mg CaCO}_3$$

$$\therefore \boxed{\text{Permanent hardness} = \left[ 1,000 \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \times S \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right] \text{mg/L}} \quad \dots(3)$$

**Step (iv) : Determination of Temporary hardness of unknown hard water :**

As  $\text{Total hardness} = \text{Permanent hardness} + \text{Temporary hardness}$

$\therefore \text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$

Using results of equations (2) and (3), above equation becomes

$$\text{Temporary hardness} = \left[ 1000 \times \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} \times S \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right] - \left[ 1000 \times \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \times S \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \right]$$

$$\text{Temporary hardness} = 1000 \times S \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \left[ \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} - \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \right] \text{mg/L} \quad \dots(4)$$

### Approach II : Based on Normality Concepts

**Step (i) : Standardization of EDTA solution :**

Suppose, for each titration, we use  $V_{\text{SHW}}^{\text{Std}}$  mL of standard hard water (SHW) for standardization (Std).

Given, 1 litre of standard hard water contains  $S$  gm  $\text{CaCO}_3$ .

$$\begin{aligned} \text{Hence, } \left[ V_{\text{SHW}}^{\text{Std}} \text{ mL or } \frac{V_{\text{SHW}}^{\text{Std}}}{1000} \text{ L} \right] & \text{ of standard hard water} \\ & = \frac{V_{\text{SHW}}^{\text{Std}} S}{1000} \text{ gm } \text{CaCO}_3 \quad \dots(i) \end{aligned}$$

$$\begin{aligned} \therefore \text{Number of gram equivalents of standard hard water (SHW)} & \\ & = \frac{\text{Weight in grams of } \text{CaCO}_3 \text{ in standard hard water}}{\text{Equivalent weight of } \text{CaCO}_3} \end{aligned}$$

$$= \frac{V_{\text{SHW}}^{\text{Std}} S / 1000}{50}$$

$$= \frac{V_{\text{SHW}}^{\text{Std}} S}{50 \times 1000} \quad \dots(ii)$$

Let, Normality of EDTA solution =  $N_{\text{EDTA}}$

Volume of EDTA solution needed for standardization

$$= V_{\text{EDTA}}^{\text{Std}} \text{ mL} = \frac{V_{\text{EDTA}}^{\text{Std}}}{1000} \text{ Litres}$$

Now, Number of gram equivalents of EDTA

$$= \frac{V_{\text{EDTA}}^{\text{Std}}}{1000} \times N_{\text{EDTA}} \quad \dots(iii)$$



At the equivalence point, during titration

$$\boxed{\begin{aligned} \text{Number of gram equivalents of EDTA} \\ = \text{Number of gram equivalents of hard water} \end{aligned}}$$

...(iv)

Using equations (ii) and (iii), equation (iv) becomes

$$\begin{aligned} \frac{V_{SHW}^{Std} S}{50 \times 1000} &= \frac{V_{EDTA}^{Std}}{1000} \times N_{EDTA} \\ \Rightarrow N_{EDTA} &= \frac{1000 S V_{SHW}^{Std}}{50 \times 1000 \times V_{EDTA}^{Std}} \end{aligned}$$

**Step (ii) : Determination of total hardness of unknown water sample :**

Let Normality of unknown hard water (UHW) whose total hardness (TH) has to be determined =  $N_{EDTA}^{TH}$

Using equation (iv) and applying Normality equation, we have :

$$\begin{aligned} N_{UHW}^{TH} \times V_{UHW}^{TH} &= N_{EDTA} \times V_{EDTA}^{TH} \\ \Rightarrow N_{UHW}^{TH} &= \frac{N_{EDTA} \times V_{UHW}^{TH}}{V_{UHW}^{TH}} \\ &= \frac{1000 S V_{SHW}^{Std} V_{EDTA}^{TH}}{50 \times 1000 \times V_{EDTA}^{Std} \times V_{UHW}^{TH}} \end{aligned}$$

As strength (in gms per litre) = Normality  $\times$  Equivalent weight  
and equivalent weight of  $\text{CaCO}_3 = 50$

$$\therefore \text{Strength of Total hardness} = \left( N_{UHW}^{TH} \times 50 \right) \text{g/L}$$

$$\Rightarrow \boxed{\text{Total hardness} = \left( N_{UHW}^{TH} \times 50 \times 1000 \right) \text{mg/L}} \quad \text{...(vii)}$$

$$\begin{aligned} \Rightarrow \text{Total hardness} &= \left( \frac{1000 S V_{SHW}^{Std} V_{EDTA}^{TH}}{50 \times 1000 \times V_{EDTA}^{Std} \times V_{UHW}^{TH}} \right) \times 50 \times 1000 \text{ mg/L} \\ &= 1000 S \frac{V_{SHW}^{Std}}{V_{EDTA}^{Std}} \times \frac{V_{EDTA}^{TH}}{V_{UHW}^{TH}} \text{ mg/L} \end{aligned}$$

$$\text{Thus, } \boxed{\text{Total hardness} = 1000 S \frac{V_{SHW}^{Std}}{V_{EDTA}^{Std}} \times \frac{V_{EDTA}^{TH}}{V_{UHW}^{TH}} \text{ ppm}} \quad \text{...(viii)}$$

**Step (iii) : Determination of permanent hardness of unknown water sample :**

Let Normality of unknown hard water (UHW) whose permanent hardness (PH) has to be determined =  $N_{UHW}^{PH}$



Using Equation (iv) and applying Normality equation, we have :

$$\begin{aligned}
 N_{UHW}^{PH} \times V_{UHW}^{PH} &= N_{EDTA} \times V_{EDTA}^{PH} \\
 \Rightarrow N_{UHW}^{PH} &= \frac{N_{EDTA} \times V_{EDTA}^{PH}}{V_{UHW}^{PH}} \\
 &= \frac{1000 S V_{SHW}^{Std}}{50 \times 1000 \times V_{EDTA}^{Std}} \times \frac{V_{EDTA}^{PH}}{V_{UHW}^{PH}} N \quad \dots(ix)
 \end{aligned}$$

Now, permanent hardness (strength) =  $(N_{UHW}^{PH} \times 50)$  g/L

$$\Rightarrow \text{Permanent hardness} = (N_{UHW}^{PH} \times 50 \times 1000) \text{ mg/L} \quad \dots(x)$$

$$\Rightarrow \text{Permanent hardness} = \left( \frac{1000 S V_{SHW}^{Std} \times V_{EDTA}^{PH}}{50 \times 1000 \times V_{EDTA}^{Std} \times V_{UHW}^{PH}} \times 50 \times 1000 \right) \text{ mg/L}$$

$$\text{Thus, Permanent hardness} = \left( 1000 S \frac{V_{SHW}^{Std}}{V_{EDTA}^{Std}} \times \frac{V_{EDTA}^{PH}}{V_{UHW}^{PH}} \right) \text{ ppm} \quad \dots(xi)$$

**Step (iv) : Determination of temporary hardness :**

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} \quad \dots(xii)$$

$$\Rightarrow \text{Temporary hardness} = 1000 S \frac{V_{SHW}^{Std}}{V_{EDTA}^{Std}} \left[ \frac{V_{EDTA}^{TH}}{V_{UHW}^{TH}} - \frac{V_{EDTA}^{PH}}{V_{UHW}^{PH}} \right] \text{ ppm}$$

### Approach III : Based on Molarity concepts

**Step (i) : Standardization of EDTA solution :**

We know that EDTA titrations are based on the 1:1 metal-EDTA complex formation.

Thus, 1 molecule of EDTA = 1 metal-ion ...(i)

Multiplying the above equation with Avogadro Number ( $6.023 \times 10^{23}$ ) on both the sides, we get

1 mole of EDTA = 1 mole of metal-ions ...(ii)

By definition, Molarity is number of moles of solute per litre of solution.

So, if we multiply Molarity with volume (in litres), we get moles.

Let, Molarity of EDTA solution =  $M_{EDTA}$

Volume of EDTA solution required for standardization

$$= V_{EDTA}^{Std} \text{ mL} = \frac{V_{EDTA}^{Std}}{1000} \text{ litres}$$



Using these concepts and abbreviations,

$$\text{Moles of EDTA} = M_{\text{EDTA}} \times \frac{V_{\text{EDTA}}^{\text{Std}}}{1000} \quad \dots(iii)$$

Given, 1 litre of standard hard water (SHW) contains =  $S$  gm of  $\text{CaCO}_3$

$$\begin{aligned} \therefore V_{\text{SHW}}^{\text{Std}} \text{ mL of standard hard water (SHW) contains} \\ = \frac{S}{1000} \times V_{\text{SHW}}^{\text{Std}} \text{ gm CaCO}_3 \end{aligned} \quad \dots(iv)$$

As Molar mass of  $\text{CaCO}_3 = 100$

$$\begin{aligned} \therefore \text{Number of Moles of metal ions in standard hard water (SHW)} \\ = \frac{\text{Weight in gms of CaCO}_3 \text{ in SHW}}{\text{Molar mass of CaCO}_3} \\ = \frac{S \times V_{\text{SHW}}^{\text{Std}}}{1000 \times 100} \end{aligned} \quad \dots(v)$$

Using equation (ii), during titration at the equivalence point :

$$\boxed{\text{Number of moles of EDTA} = \text{Number of moles of hard water}} \quad \dots(vi)$$

Using equations (iii) and (v), equation (vi) becomes

$$\begin{aligned} M_{\text{EDTA}} \times \frac{V_{\text{EDTA}}^{\text{Std}}}{1000} &= \frac{S \times V_{\text{SHW}}^{\text{Std}}}{1000 \times 100} \\ \Rightarrow M_{\text{EDTA}} &= \frac{S \times V_{\text{SHW}}^{\text{Std}}}{1000 \times 100} \times \frac{1000}{V_{\text{EDTA}}^{\text{Std}}} M \\ &= \frac{S}{100} \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} M \end{aligned} \quad \dots(vii)$$

**Step (ii) : Determination of total hardness of unknown hard water sample :**

Let Molarity of unknown hard water (UHW) whose total hardness (TH) has to be determined =  $M_{\text{UHW}}^{\text{TH}}$

And suppose for each titration during total hardness determination, we use  $V_{\text{UHW}}^{\text{TH}}$  mL of unknown hard water.

Using equation (vi) and applying Molarity equation, we have :

$$\begin{aligned} \boxed{M_{\text{UHW}}^{\text{TH}} \times V_{\text{UHW}}^{\text{TH}} = M_{\text{EDTA}} \times V_{\text{EDTA}}^{\text{TH}}} \quad \dots(viii) \\ \Rightarrow M_{\text{UHW}}^{\text{TH}} = M_{\text{EDTA}} \times \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} \end{aligned}$$

$$\Rightarrow = \frac{S}{100} \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \times \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} M \quad \dots(ix)$$



As strength (in grams per litre) = Molarity  $\times$  Molar mass

And Molar mass of  $\text{CaCO}_3 = 100$

$$\therefore \text{Strength of total hardness} = (M_{\text{UHW}}^{\text{TH}} \times 100) \text{ g/L}$$

$$\Rightarrow \text{Total hardness} = (M_{\text{UHW}}^{\text{TH}} \times 100) \text{ g/L}$$

$$\Rightarrow \text{Total hardness} = (M_{\text{UHW}}^{\text{TH}} \times 100 \times 1000) \text{ mg/L} \quad \dots(x)$$

$$\therefore \text{Total hardness} = 1000 S \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \times \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} \text{ ppm} \quad \dots(xi)$$

**Step (iii) : Determination of permanent hardness of unknown hard water sample :**

Let Molarity of unknown hard water (UHW) whose permanent hardness (PH) has to be determined =  $M_{\text{UHW}}^{\text{PH}}$

And suppose for each titration, during permanent hardness determination, we used  $V_{\text{UHW}}^{\text{PH}}$  mL of unknown hard water.

Using equation (vi) and applying Molarity equation, we have

$$\Rightarrow M_{\text{UHW}}^{\text{PH}} \times V_{\text{UHW}}^{\text{PH}} = M_{\text{EDTA}} \times V_{\text{EDTA}}^{\text{PH}} \quad \dots(xii)$$

$$\begin{aligned} M_{\text{UHW}}^{\text{PH}} &= M_{\text{EDTA}} \times \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \\ &= \frac{S}{100} \times \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \times \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} M \quad \dots(xiii) \end{aligned}$$

$$\text{Now, Permanent hardness} = (M_{\text{UHW}}^{\text{PH}} \times 100) \text{ g/L}$$

$$\Rightarrow \text{Permanent hardness} = (M_{\text{UHW}}^{\text{PH}} \times 100 \times 1000) \text{ mg/L} \quad \dots(xiv)$$

$$\therefore \text{Permanent hardness} = 1000 S \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \times \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \text{ ppm} \quad \dots(xv)$$

**Step (iv) : Determination of temporary hardness :**

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} \quad \dots(xvi)$$

$$\Rightarrow \text{Temporary hardness} = 1000 S \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \left( \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} - \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \right) \text{ ppm}$$

**Advantages of EDTA method :** Advantages of EDTA method for hardness determination are its greater accuracy, convenience and more rapid procedure.



**Significance of hardness determination :** The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses. The test is particularly important to industry because when hard water is heated, it precipitates calcium carbonate, which then clogs boilers and pipes.

### 6.1 Solved Examples based on Determination of Hardness by EDTA Method

**Example 1.** 0.28 g of  $\text{CaCO}_3$  was dissolved in HCl and the solution was made to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of the hard water sample required 35 ml of the same EDTA solution on titration. After boiling 100 ml of this water, Cooling, Filtering and then Titration required 10 ml of EDTA solution. Calculate the temporary and permanent hardness of water.

**Solution.** Step (i) Standardization of EDTA solution :

Given, 1 L of standard hard water contains 0.28 gm  $\text{CaCO}_3$ . Hence, each mL of standard hard water contains 0.28 mg  $\text{CaCO}_3$

As, 28 mL of EDTA = 100 mL of standard hard water  
 $= 100 \times 0.28 = 28 \text{ mg } \text{CaCO}_3$

$$\therefore 1 \text{ mL of EDTA} = \frac{28}{28} = 1 \text{ mg } \text{CaCO}_3 \quad \dots(i)$$

Step (ii) Determination of total hardness of water :

Given, 100 mL of unknown hard water sample = 35 mL of EDTA  
 $= 35 \times 1 = 35 \text{ mg } \text{CaCO}_3$

{By using (i)}

$\therefore$  1,000 mL (or 1L) of unknown hard water sample

$$= \frac{35}{100} \times 1000 = 350 \text{ mg } \text{CaCO}_3 \text{ eq. hardness}$$

Hence, Total hardness = 350 ppm

...(ii)

Step (iii) Determination of permanent hardness

100 mL of boiled water = 10 mL of EDTA

$$= 10 \times 1 = 10 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$\therefore$  1,000 mL (or 1 L) of boiled water

$$= \frac{10}{100} \times 1000 = 100 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

Hence, Permanent hardness of water = 100 ppm

...(iii)

Step (iv) Determination of Temporary hardness

$$\begin{aligned} \text{Temporary hardness} &= \text{Total hardness} - \text{Permanent hardness} \\ &= 350 - 100 \end{aligned}$$

$$\Rightarrow \text{Temporary hardness} = 250 \text{ ppm}$$

...(iv)

### Alternative Solution

$$(i) \text{ Total hardness} = 1000 \times \frac{V_{\text{Std}}^{\text{SHW}}}{V_{\text{EDTA}}^{\text{Std}}} \times \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} \text{ ppm}$$

$$= 1000 \times 0.28 \times \frac{100}{28} \times \frac{35}{100} = 350 \text{ ppm}$$

...(1)

$$= 1000 \times 0.28 \times 3.57 \times 0.35 = 350$$

$$\begin{aligned}
 \text{(ii) Permanent hardness} &= 1000 \times \frac{V_{\text{Std SHW}}}{V_{\text{EDTA}}^{\text{Std}}} \times \frac{V_{\text{EDTA}}^{\text{PH}}}{V_{\text{UHW}}^{\text{PH}}} \\
 &= 1000 \times 0.28 \times \frac{100}{28} \times \frac{10}{100} = 100 \text{ ppm} \quad \dots(2)
 \end{aligned}$$

$$\begin{aligned}
 \text{(iii) Temporary hardness} &= \text{Total hardness} - \text{Permanent hardness} \\
 &= 350 - 100 = 250 \text{ ppm} \quad \dots(3)
 \end{aligned}$$

**Example 2.** A standard hard water contains 1000 mg of  $\text{CaCO}_3$  per liter. 50 ml of this required 50 ml of EDTA solution, 50 ml of sample water required 40 ml of EDTA solution. The sample after boiling required 20 ml EDTA solution. Calculate the temporary and permanent hardness of the given sample of water, in different units.

[RGPV, June 2002, June 2003]

**Solution.** Step (i) Standardization of EDTA solution :

Given 1 L of standard hard water contains 1000 mg  $\text{CaCO}_3$

$\therefore$  1 mL of standard hard water contains 1 mg  $\text{CaCO}_3$

Now 50 mL of EDTA = 50 mL of standard hard water  
 $= 50 \times 1 = 50 \text{ mg of } \text{CaCO}_3$

$\Rightarrow$  1 mL of EDTA =  $\frac{50}{50} = 1 \text{ mg of } \text{CaCO}_3$  equivalent hardness

Step (ii) Determination of total hardness of water :

50 mL of sample water = 40 mL of EDTA

$= 40 \times 1 = 40 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

$\therefore$  1 L of sample water =  $\frac{40}{50} \times 1000 = 800 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

Hence, total hardness of water = 800 ppm

...(ii)

Step (iii) Determination of Permanent hardness

50 mL of boiled water = 20 mL of EDTA

$= 20 \times 1 = 20 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

$\therefore$  1 L of boiled water =  $\frac{20}{50} \times 1000 = 400 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

Hence, permanent hardness of water = 400 ppm

...(iii)

Step (iv) Determination of Temporary hardness

Temporary hardness = Total hardness - Permanent hardness

$= 800 - 400 = 400 \text{ ppm}$

$\therefore$  Temporary hardness = 400 ppm =  $400 \times 0.1 = 40^\circ \text{Fr}$

$= 400 \times 0.07 = 28^\circ \text{Cl}$

...(iv)

**Example 3.** 50 ml of standard hard water containing 1.5 mg of pure  $\text{CaCO}_3$  per ml consumed 44 ml of EDTA. 40 ml of a water sample consumed 20 ml of the same EDTA solution. Using eriochrome T as indicator, calculate the total hardness of water sample in ppm,  $^\circ \text{Cl}$  and  $^\circ \text{Fr}$ .

[RGPV, Feb. 2005]



**Solution. Step (i) Standardization of EDTA solution**

Given 1 mL of standard hard water contains 1.5 mg  $\text{CaCO}_3$

Now 44 mL of EDTA = 50 mL of standard hard water  
 $= 50 \times 1.5 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

Hence, 1 mL of EDTA  $= \frac{50 \times 1.5}{44} = 1.7 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness} \quad \dots(i)$

**Step (ii) Determination of total hardness of water sample**

40 mL of sample water = 20 mL of EDTA  
 $= 20 \times 1.7 = 34 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

Hence, 1 L of sample water  $= \frac{34}{40} \times 1000 = 850 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

Thus, total hardness of water  $= 850 \text{ ppm} = 850 \times 0.1 = 85^\circ \text{Fr} \quad \dots(ii)$   
 $= 850 \times 0.07 = 59.5^\circ \text{Cl}$

**Alternative solution :**

$$\text{Total hardness} = 1000 S \frac{V_{\text{SHW}}^{\text{Std}}}{V_{\text{EDTA}}^{\text{Std}}} \times \frac{V_{\text{EDTA}}^{\text{TH}}}{V_{\text{UHW}}^{\text{TH}}} \text{ ppm} \quad \dots(iii)$$

$$= 1000 \times 1.5 \times \frac{50}{44} \times \frac{20}{40}$$

$$= 850 \text{ ppm}$$

$$= 850 \times 0.1 = 85^\circ \text{Fr} \quad \dots(iv)$$

$$= 850 \times 0.07 = 59.5^\circ \text{Cl}$$

**Example 4.** Calculate the hardness of a water sample, whose 10 ml required 10 ml of EDTA. 20 ml of  $\text{CaCl}_2$  solution, whose strength is equivalent 1.5 g of  $\text{CaCO}_3$  per litre, required 30 ml of EDTA solution.

**Solution. Step (i) Standardization of EDTA solution**

Given 1 L of standard hard water contains = 1.5 gm  $\text{CaCO}_3$

$\therefore$  1 mL of standard hard water contains = 1.5 mg  $\text{CaCO}_3$

Now, 30 mL of EDTA = 20 mL of standard hard water (i.e.,  $\text{CaCl}_2$  solution)  
 $= 20 \times 1.5 = 30 \text{ mg } \text{CaCO}_3$

So, 1 mL of EDTA  $= \frac{30}{30} = 1 \text{ mg } \text{CaCO}_3 \text{ eq. hardness} \quad \dots(i)$

**Step (ii) Determination of Total hardness of water :**

10 mL of sample water = 10 mL of EDTA  
 $= 10 \times 1 = 10 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

$\therefore$  1 L of sample water  $= \frac{10}{10} \times 1000 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$

Hence, the total hardness of water sample = 1000 ppm.

**Example 5.** Standard hard water contains 1 g of  $\text{CaCO}_3$  per litre. 100 ml of this required 25 ml of EDTA solution for titration using EBT as an indicator. Further 100 ml of sample hard water required 30 ml of the same EDTA solution for titration. The sample water was then boiled. 100 ml of the boiled water now required 10 ml of the same EDTA

solution for titration. Calculate total hardness, permanent hardness as well as temporary hardness in the given sample of hard water. Report the values in terms of ppm.

[GGSIPU, 1st Term, Sept. 2005]

**Solution.**  $M_{\text{SHW}} = \frac{1 \text{ g/100 g mol}^{-1}}{1 \text{ L}} = 0.01 \text{ M}$

(i)  $25 \text{ ml} \times M_{\text{EDTA}} = 100 \text{ ml} \times M_{\text{SHW}}$

$\Rightarrow$  Molarity of EDTA  $= M_{\text{EDTA}} = \frac{100 \times 0.01}{25} = \frac{1}{25} \text{ M}$

(ii)  $100 \text{ ml} \times M_{\text{UHW}}^{\text{TH}} = \frac{1}{25} \times 30 \text{ ml}$

$\therefore$  Total hardness (TH)  $= M_{\text{UHW}}^{\text{TH}} \times 100 \times 1000 \text{ mg/L}$   
 $= \frac{1}{25} \times 30 \times \frac{1}{100} \times 10^5 = \frac{30,000}{25} \text{ ppm} = 1200 \text{ ppm.}$

(iii)  $100 \text{ ml} \times M_{\text{UHW}}^{\text{PH}} = \frac{1}{25} \times 10$

$\therefore$  Permanent hardness (PH)  $= M_{\text{UHW}}^{\text{PH}} \times 10^5 \text{ ppm}$   
 $= \frac{1}{25} \times 10 \times \frac{1}{100} \times 10^5 = \frac{10,000}{25} = 400 \text{ ppm.}$

(iv) Temporary hardness  $= \text{TH} - \text{PH}$   
 $= 1200 - 400 = 800 \text{ ppm.}$

## 7 ALKALINITY

**Theory.** By alkalinity of water we mean the total content of those substances in it which causes an increased hydroxide ion concentration  $[\text{OH}^-]$  upon dissociation or due to hydrolysis. The alkalinity of water is attributed to the presence of the:

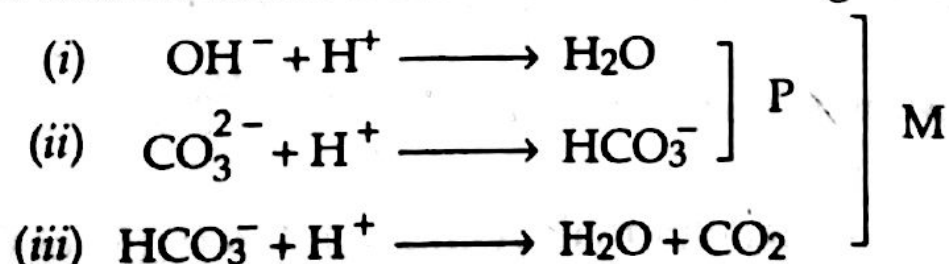
(i) caustic alkalinity (due to  $\text{OH}^-$  to  $\text{CO}_3^{2-}$  ions), and

(ii) temporary hardness (due to  $\text{HCO}_3^-$  ions).

Alkalinity is a measure of the ability of water to neutralize the acids.

$\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators.

The determination is based on the following reactions:



The titration of the water sample against a standard acid upto phenolphthalein end-point (P) marks the completion of reactions (i) and (ii) only. This amount of acid used thus corresponds to hydroxide plus one-half of the normal carbonate present.

On the other hand, titration of the water sample against a standard acid to methyl orange end-point (M) marks the completion of reactions (i), (ii) and (iii).



Hence the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions).

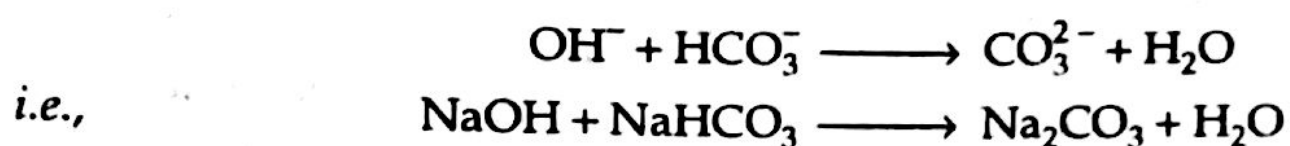
Thus,  $P = \text{OH}^- \text{ and } \frac{1}{2} \text{CO}_3^{2-}$

and  $M = \text{OH}^-, \text{CO}_3^{2-}, \text{HCO}_3^-$

With respect to the constituents causing alkalinity in water, the following situations may arise :

- (i)  $\text{OH}^-$  only      (ii)  $\text{CO}_3^{2-}$  only      (iii)  $\text{HCO}_3^-$  only  
 (iv)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  together      (v)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  together.

The possibility of  $\text{OH}^-$  and  $\text{HCO}_3^-$  together is ruled out, because of the fact that they combine instantaneously to form  $\text{CO}_3^{2-}$  ions.



Thus,  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions cannot exist together in water.

On the basis of same reasoning, all the three ( $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) cannot exist together.

#### Procedure :

Pipette out 100 mL of the water sample in a clean titration flask. Add to it 2 to 3 drops of a *phenolphthalein* indicator. Run in N/50  $\text{H}_2\text{SO}_4$  (from a burette), till the pink colour is just discharged. Let the volume of acid used to phenolphthalein end point =  $V_1$  mL. Then to the same solution, add 2 or 3 drops of *methyl orange*. Continue the titration, till the pink colour reappears. Let *extra volume* of acid used to methyl orange end point =  $V_2$  mL.

#### Calculations :

100 mL of water upto phenolphthalein end-point  
 $\equiv V_1$  mL of N/50  $\text{H}_2\text{SO}_4$

$$\therefore 100 \text{ mL} \times N_p = V_1 \text{ mL} \times (N/50)$$

or normality, 
$$N_p = \frac{V_1 \text{ mL}}{100 \text{ mL}} \times \frac{N}{50} = \frac{V_1}{5000} N.$$

Note : Normality (N) =  $\frac{\text{gm. Eq.}}{L} = \frac{x/\text{Eq. wt.}}{L}$  ; where x = weight in gms.

$$\Rightarrow \text{strength} \left( \frac{x}{L} \right) = N \times \text{Eq. wt. and Eq. wt. of } \text{CaCO}_3 = \frac{\text{Mol. wt.}}{2} = \frac{100}{2} = 50.$$

$\therefore$  Strength of alkalinity upto phenolphthalein end-point in terms of  $\text{CaCO}_3$  equivalent

$$\begin{aligned} &= \frac{V_1}{5000} \times (50 \text{ g/L}) \times 1000 \frac{\text{mg}}{\text{g}} \\ P &= 10 V_1 \frac{\text{mg}}{\text{L}} = 10 V_1 \text{ ppm} \end{aligned}$$

Now 100 mL of water upto methyl orange end-point  
 $\equiv (V_1 + V_2)$  mL of  $N/50 \text{ H}_2\text{SO}_4$

$$\therefore 100 \text{ mL} \times N_M = (V_1 + V_2) \text{ mL} \times N/50$$

or normality,  $N_M = \frac{(V_1 + V_2) \text{ mL}}{100 \text{ mL}} \times N/50 = \frac{(V_1 + V_2)}{5000} N$

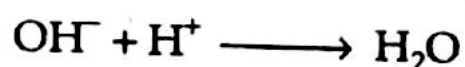
$\therefore$  Strength of total alkalinity in terms of  $\text{CaCO}_3$  eq.

$$= \frac{(V_1 + V_2)}{5000} \times 50 \text{ g/L} \times 1000 \frac{\text{mg}}{\text{g}}$$

$$M = 10 (V_1 + V_2) \frac{\text{mg}}{\text{L}} = 10 (V_1 + V_2) \text{ ppm}$$

1. Consider a case when the given water sample is alkaline due to the presence of  $\text{OH}^-$  ions only.

Both phenolphthalein as well as methyl orange indicators are suitable for detection of end point. Irrespective of the indicator, same volume (say  $V_1$  mL) of standard acid (say  $N/50 \text{ H}_2\text{SO}_4$ ) will be needed for the neutralization of  $\text{OH}^-$  ions as per the following 1:1 neutralization reaction :

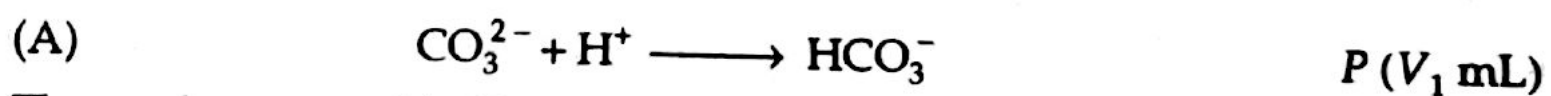


Thus,  $P = M = 10 V_1$  ppm.

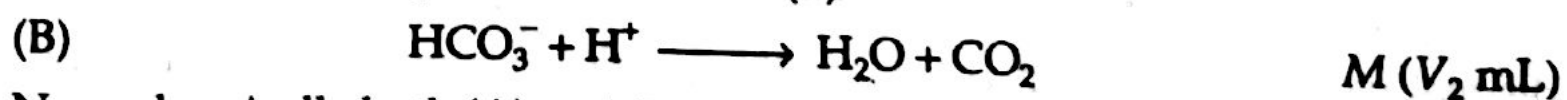
So, we can conclude that whenever  $P = M$ , the given water sample will be alkaline due to the presence of  $\text{OH}^-$  ions only and to the extent of  $P$  or  $M$  or  $10 V_1$  ppm.

2. Consider a second case when the given water sample is alkaline due to the presence of  $\text{CO}_3^{2-}$  ions only.

The titration of this alkaline water sample against a standard acid (say  $N/50 \text{ H}_2\text{SO}_4$ ) upto phenolphthalein end-point marks the completion of reaction (A) only. Let the volume of acid used =  $V_1$  mL.



Thus, when one adds  $V_1$  mL of standard acid into conical flask containing alkaline water, the pink colour will disappear. Then to the same solution, add 2 or 3 drops of methyl orange indicator. The contents of the conical flask will turn yellow. Continue the titration by adding standard acid from the burette, till either the pink colour reappears or colour changes from yellow to orange. Let extra volume of standard acid used to methyl orange end point =  $V_2$  mL. This amount of acid used marks the completion of reaction (B).



Now, chemically both (A) and (B) reactions are 1:1 neutralization reactions so same volume of acid must be needed for the neutralization.

i.e.,  $V_1 = V_2$  ... (i)

As  $P = 10 V_1$  ppm ... (ii)

and  $M = 10 (V_1 + V_2)$  ppm



but

$$V_1 = V_2$$

$$\therefore M = 10 (V_1 + V_1) = 20 V_1 \text{ ppm} \quad \dots(iii)$$

From equations (i), (ii) and (iii), we can conclude that whenever

$$P = \frac{1}{2} M$$

or

$$V_1 = V_2,$$

the given water sample is alkaline due to the presence of  $\text{CO}_3^{2-}$  ions only and to the extent of either  $M$  ppm or  $2 P$  ppm.

3. Consider a third case when the given water sample is alkaline due to the presence of  $\text{HCO}_3^-$  ions only.

For the detection of  $\text{HCO}_3^-$  ions and for the estimation of alkalinity due to  $\text{HCO}_3^-$  ions, phenolphthalein indicator is not suitable. However, alkalinity can be estimated by using methyl orange as indicator for the detection of end point.

The titration of this alkaline water sample against a standard acid to methyl orange end-point (change of colour from yellow to orange) marks the completion of following neutralization reaction



On the addition of say  $V_2$  mL of standard acid.

Thus, in this case,

$$V_1 = 0 \quad \text{or} \quad P = 0$$

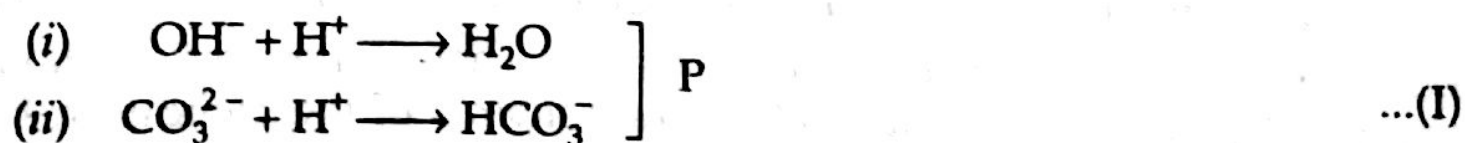
and

$$M = 10 V_2 \text{ ppm}$$

So, we can conclude that when  $P = 0$ , both  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions are absent and alkalinity is due to  $\text{HCO}_3^-$  ions only.

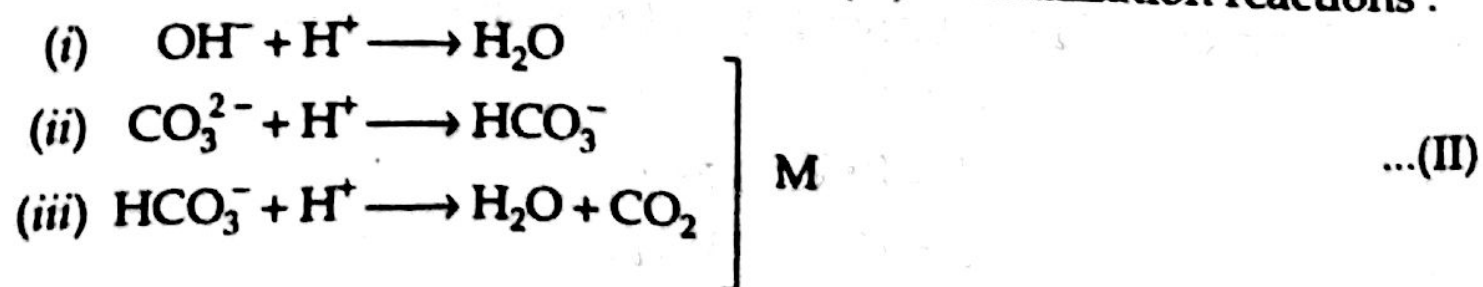
4. Consider a fourth case, when the given water sample is alkaline due to the simultaneous presence of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions.

The titration of this water sample against a standard acid upto phenolphthalein end-point ( $P$ ) marks the complete neutralization of  $\text{OH}^-$  ions and neutralization of  $\text{CO}_3^{2-}$  ions till bicarbonate ion stage only ; corresponding to following (i) and (ii) neutralization reactions.

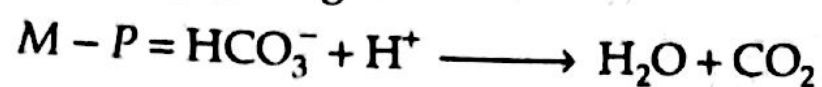


Let the volume of acid used to phenolphthalein end point =  $V_1$  mL. This amount of acid used thus corresponds to hydroxide plus one-half of the total carbonate ions present.

On the other hand, the titration of the same water sample against a standard acid upto methyl orange end-point ( $M$ ) marks the complete neutralization of both  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions ; corresponding to following (i), (ii) and (iii) neutralization reactions :



Subtracting (I) from (II), we get



And  $\text{HCO}_3^-$  ions are nothing but neutralization product of  $\text{CO}_3^{2-}$  ions till half-stage.

Thus, half of  $\text{CO}_3^{2-}$  ions equal to  $(M - P)$ .

So,  $\text{alkalinity due to complete } \text{CO}_3^{2-} = 2(M - P)$ .

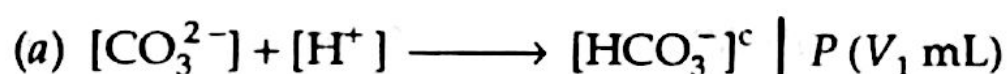
In this case, the given water sample was alkaline due to  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions and total alkalinity was estimated using methyl orange end-point ( $= M$ ).

$$\therefore \text{alkalinity due to } \text{OH}^- = M - 2(M - P)$$

$$\Rightarrow \text{alkalinity due to } \text{OH}^- = 2P - M$$

5. Consider a fifth case, when the given water sample is alkaline due to the simultaneous presence of  $\text{CO}_3^{2-}$  ions and  $\text{HCO}_3^-$  ions.

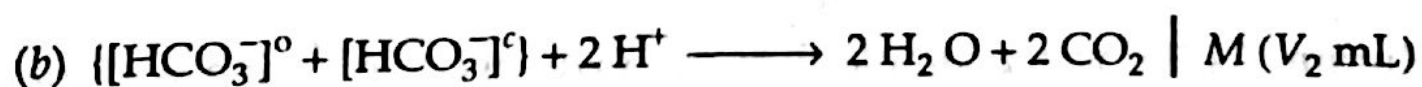
The titration of this water sample against a standard acid upto phenolphthalein end-point ( $P$ ) marks the neutralization of  $\text{CO}_3^{2-}$  ions till bicarbonate stage only ; corresponding to following neutralization reaction (a).



Let the volume of acid used to phenolphthalein end-point (change of colour from pink to colourless) =  $V_1$  mL.

Then to the same solution, add 2 or 3 drops of methyl orange. The contents will now have yellow colour. Continue the titration by adding more volume of standard acid from burette till the colour changes to pink (or orange). Let extra volume of acid used to methyl orange end point =  $V_2$  mL.

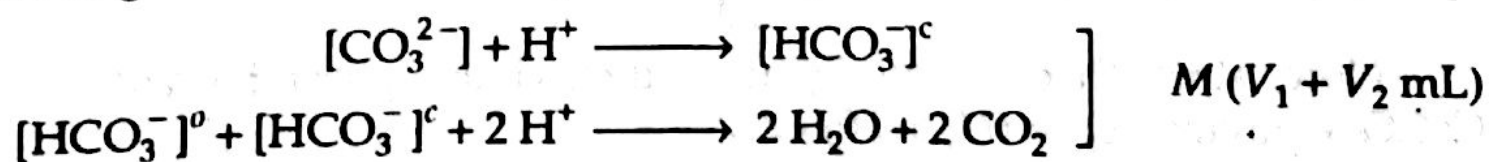
This extra volume of acid added will lead to neutralization of both the  $\text{HCO}_3^-$  ions (i.e., the  $[\text{HCO}_3^-]^o$  ions which were originally present and those  $[\text{HCO}_3^-]^c$  ions which were formed during reaction (a) above by half-neutralization of  $\text{CO}_3^{2-}$  ions.)



From reactions (a) and (b), we can conclude that

$$V_1 < V_2$$

If a separate titration of the given alkaline water sample was done using methyl orange as indicator, then complete neutralization of both  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions might have occurred as per following reactions :



Thus, numerical value of  $M$  tells us the total alkalinity.

From equation (a), numerical value of  $P$  tells us alkalinity due to half of the carbonate ions.

$$\therefore \text{alkalinity due to } \text{CO}_3^{2-} = 2P$$



and  $\text{alkalinity due to } \text{HCO}_3^- = M - 2P$

Furthermore, as  $P = 10 V_1$  ppm

and  $M = 10 (V_1 + V_2)$  ppm

since  $V_1 < V_2$

Thus,  $P < \frac{1}{2} M$

So, we can conclude that whenever  $V_1 < V_2$  or  $P < \frac{1}{2} M$ , the given water sample is alkaline due to the simultaneous presence of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions.

The results may be summarized in following Table 4 :

Table 4

S.No.	Results of Titrations	Alkalinity due to		
		Hydroxide ( $\text{OH}^-$ )	Carbonate ( $\text{CO}_3^{2-}$ )	Bicarbonate ( $\text{HCO}_3^-$ )
1.	$P = 0$	Nil	Nil	M
2.	$P = M$	P or M	Nil	Nil
3.	$P = \frac{1}{2} M$ (or $V_1 = V_2$ )	Nil	2P	Nil
4.	$P > \frac{1}{2} M$ (or $V_1 > V_2$ )	(2P - M)	2 (M - P)	Nil
5.	$P < \frac{1}{2} M$ (or $V_1 < V_2$ )	Nil	2P	M - 2P

#### Drawbacks of using Highly alkaline water

- (a) It may lead to caustic embrittlement,
- (b) It may lead to deposition of precipitates and sludges in boiler tubes and pipes.

#### 7.1 Solved Examples based on Determination of Alkalinity of Water

**Example 1.** 50 mL of a sample of water required 5 mL of N/50  $\text{H}_2\text{SO}_4$  using methyl orange as indicator but did not give any colouration with phenolphthalein. What type of alkalinity is present? Express the same in ppm.

**Solution.** As the water sample does not give any colouration with phenolphthalein ( $P = 0$ ), hence only  $\text{HCO}_3^-$  ions are present.

Now, 50 mL of water sample upto methyl orange end-point = 5 mL of N/50  $\text{H}_2\text{SO}_4$

$$\therefore 50 \text{ mL} \times N_M = 5 \text{ mL} \times N/50$$

$$\text{or Normality, } N_M = 5 \text{ mL} \times \frac{N}{50} \times \frac{1}{50 \text{ mL}} = \frac{1}{500} N$$

Now, strength of alkalinity upto methyl orange end point (in terms of  $\text{CaCO}_3$  equivalents) =  $(N_M \times 50)$  g/L

$$\Rightarrow M = \frac{1}{500} \times 50 \text{ g/L} \times 1000 \text{ gm/g}$$

$$\Rightarrow M = 100 \text{ mg/L} = 100 \text{ ppm.}$$

Hence, alkalinity due to  $\text{HCO}_3^- = M = 100 \text{ ppm}$

**Example 2.** 200 mL of water sample, on titration with  $N/50$   $H_2SO_4$  using phenolphthalein as indicator, gave the end point when 10 mL of acid were run down. Another lot of 200 mL of the sample also required 10 mL of the acid to obtain methyl-orange end point. What type of alkalinity is present in the sample and what is its magnitude?

**Solution.** 200 mL of water upto phenolphthalein end point

$$\equiv 10 \text{ mL of } \frac{N}{50} H_2SO_4$$

$$\therefore 200 \text{ mL} \times N_p = 10 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality, } N_p = 10 \text{ mL} \times \frac{1}{50} \times \frac{1}{200 \text{ mL}} N = \frac{1}{1000} N$$

$$\text{Hence, } P = N_p \times 50 \times 1000 \text{ ppm}$$

$$= \frac{1}{1000} \times 50 \times 1000 = 50 \text{ ppm}$$

$$\text{Similarly, } M = 50 \text{ ppm}$$

From equations (1) and (2), As  $P = M$

Hence, only  $OH^-$  ions are present which are causing alkalinity, and alkalinity due to  $OH^- = 50 \text{ ppm}$ .

**Example 3.** 500 mL of a water sample, on titration with  $N/50$   $H_2SO_4$  gave a titre value of 29 mL to phenolphthalein end point and another 500 mL sample on titration with same acid gave a titre value of 58 mL to methyl orange end point. Calculate the alkalinity of the water sample in terms of  $CaCO_3$  and comment on the type of alkalinity present.

**Solution.** 500 mL of water upto phenolphthalein end-point

$$\equiv 29 \text{ mL of } \frac{N}{50} H_2SO_4$$

$$\therefore 500 \text{ mL} \times N_p = 29 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality, } N_p = \frac{29 \text{ mL}}{500 \text{ mL}} \times \frac{1}{50} N$$

Now, strength of alkalinity upto phenolphthalein end-point in terms of  $CaCO_3$  equivalent =  $N_p \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow P = 58 \text{ ppm} \quad \dots(i)$$

Given, 500 mL of water upto methyl orange end-point  $\equiv 58 \text{ mL of } \frac{N}{50} H_2SO_4$

$$\therefore 500 \text{ mL} \times N_M = 58 \text{ mL} \times \frac{N}{50}$$

$$\Rightarrow \text{Normality, } N_M = \frac{58 \text{ mL}}{500 \text{ mL}} \times \frac{1}{50} N$$

Now, strength (in terms of  $CaCO_3$  equivalents) =  $M = N_M \times 50 \times 1000 \text{ ppm}$

$$M = 116 \text{ ppm} \quad \dots(ii)$$



From equations (i) and (ii);  $P = \frac{1}{2} M$

Hence, only  $\text{CO}_3^{2-}$  ions are present

And Alkalinity of water sample due to  $\text{CO}_3^{2-} = 2P = M = 116 \text{ ppm}$ .

**Example 4.** A sample of water was alkaline to both phenolphthalein and methyl orange. 100 mL of this water sample required 12.4 mL of N/50  $\text{H}_2\text{SO}_4$  for phenolphthalein end point and 15.2 mL of the acid to methyl orange end point. Determine the types and extent of alkalinity present. [RGPV, June 2001]

**Solution.** 100 mL of water upto phenolphthalein end-point = 12.4 mL of  $\frac{N}{50} \text{H}_2\text{SO}_4$

$$\therefore 100 \text{ mL} \times N_p = 12.4 \text{ mL} \times \frac{N}{50}$$

or Normality  $N_p = \frac{12.4 \text{ mL}}{100 \text{ mL}} \times \frac{1}{50} N$

Now, strength of alkalinity upto phenolphthalein end-point in terms of  $\text{CaCO}_3$  equivalent =  $N_p \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow P = \frac{12.4}{100} \times \frac{1}{50} \times 50 \times 1000 = 12.4 \text{ ppm}$$

$$\Rightarrow P = 12.4 \text{ ppm}$$

...(i)

As, 100 mL of water upto methyl orange end-point

$$15.2 \text{ mL of } \frac{N}{50} \text{H}_2\text{SO}_4$$

$$\therefore 100 \text{ mL} \times N_M = 15.2 \text{ mL} \times \frac{N}{50}$$

or Normality,  $N_M = \frac{15.2 \text{ mL}}{100 \text{ mL}} \times \frac{1}{50} N$

Hence, strength (in terms of  $\text{CaCO}_3$  equivalents) =  $M = N_M \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow M = 15.2 \text{ ppm}$$

...(ii)

Since  $P > \frac{1}{2} M$ . Hence  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions are present.

and Alkalinity due to  $\text{OH}^- = 2P - M = 2 \times 12.4 - 15.2 = 9.6 \text{ ppm}$

and Alkalinity due to  $\text{CO}_3^{2-} = 2(M - P) = 2(15.2 - 12.4) = 5.6 \text{ ppm}$

Hence, the given water sample contains :  $\text{OH}^-$  Alkalinity = 9.6 ppm

$\text{CO}_3^{2-}$  Alkalinity = 5.6 ppm

**Example 5.** A Water sample is alkaline to both phenolphthalein as well as methyl orange. 200 mL of water sample on titration with N/50 HCl required 9.4 mL of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and the titration further continued, the yellow colour of the solution just turned red after addition of another 21 mL of the acid solution. Elucidate on the type and extent of alkalinity present in the water.

**Solution.** 200 mL of water upto phenolphthalein end-point  
= 9.4 mL of N/50 HCl

$$\therefore 200 \text{ mL} \times N_p = 9.4 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality, } N_p = \frac{9.4 \text{ mL}}{200 \text{ mL}} \times \frac{1}{50} N$$

Now, strength of alkalinity upto phenolphthalein end-point in terms of  $\text{CaCO}_3$  equivalent =  $P = N_p \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow P = 47 \text{ ppm} \quad \dots(i)$$

As, 200 mL of water upto methyl orange end point

$$= 9.4 + 21 = 30.4 \text{ mL of } N/50 \text{ HCl}$$

$$\therefore 200 \text{ mL} \times N_M = 30.4 \text{ mL} \times N/50$$

$$\text{or Normality, } N_M = \frac{30.4 \text{ mL}}{200 \text{ mL}} \times \frac{1}{50} N$$

Hence, strength of alkalinity upto methyl orange end-point in terms of  $\text{CaCO}_3$  equivalent hardness

$$= M = N_M \times 50 \times 1000 \text{ ppm}$$

$$\Rightarrow M = 152 \text{ ppm} \quad \dots(ii)$$

Since  $P < \frac{1}{2} M$ . Hence  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions are present.

and Alkalinity due to  $\text{CO}_3^{2-} = 2P = 2 \times 47 = 94 \text{ ppm}$

and Alkalinity due to  $\text{HCO}_3^- = M - 2P = 152 - 94 = 58 \text{ ppm}$

Hence, the given water sample contains  $\text{CO}_3^{2-}$  alkalinity = 94 ppm

and  $\text{HCO}_3^-$  alkalinity = 58 ppm.

**Example 6.** 250 mL of a sample of water requires 4.5 mL of 0.1 N  $\text{H}_2\text{SO}_4$  for complete neutralization using methyl orange as indicator. Another 250 mL of the same sample of water was boiled with exactly 50 mL of 0.1 N alkali mixture. After filtering off the precipitate, the filtrate was made up to exactly 250 mL. 50 mL of this made up solution requires 8.5 mL of 0.1 N  $\text{H}_2\text{SO}_4$  for complete neutralization. Calculate the carbonate, non-carbonate and total hardness of the water sample.

**Solution.** (i) In the absence of hydroxide alkalinity, the carbonate hardness is determined by titration against standard strong acid using methyl orange indicator. Thus, titration upto methyl orange end point indicates the carbonate hardness or carbonate alkalinity.

250 mL of water upto methyl orange end-point = 4.5 mL of 0.1 N  $\text{H}_2\text{SO}_4$

$$\therefore 250 \text{ mL} \times N_M = 4.5 \text{ mL} \times 0.1 N$$

$$\Rightarrow \text{Normality of water (} N_M \text{)} = \frac{4.5 \times 0.1}{250} = 1.8 \times 10^{-3} N$$

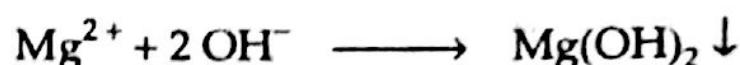
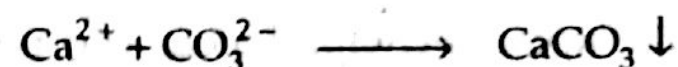
Now, strength of hardness upto methyl orange end-point in terms of  $\text{CaCO}_3$  equivalent  $M = N_M \times 50 \times 1000 \text{ ppm} = 90 \text{ ppm}$

so carbonate hardness (in terms of  $\text{CaCO}_3$  equivalents) = 90 ppm  $\dots(a)$



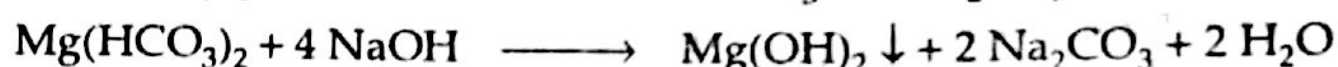
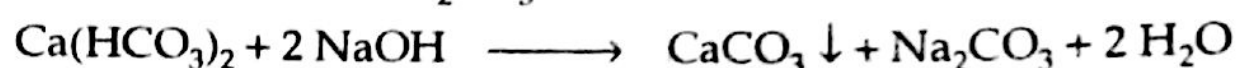
(ii) For the estimation of non-carbonate hardness,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  of Ca and Mg are precipitated by boiling the water sample with a known excess of a mixture of NaOH and  $\text{Na}_2\text{CO}_3$  (known as alkali mixture or soda reagent).

The involved reactions are :



Then precipitates are filtered off and the unused alkali mixture is back titrated against standard acid.

Note that even if the bicarbonates of Ca and Mg are present, they are converted into equivalent amounts of  $\text{Na}_2\text{CO}_3$ .



Thus, no alkali is consumed by the carbonate hardness present. However, in practice, the carbonate hardness is removed by boiling prior to the addition of the alkali mixture.

Assuming there is no non carbonate hardness. As 50 mL of 0.1 N alkali mixture was made up to 250 mL, so the normality of this made up solution

$$= \frac{50 \text{ mL} \times 0.1 \text{ N}}{250 \text{ mL}} = 0.02 \text{ N} \quad \dots(b)$$

But given 50 mL of made up solution requires 8.5 mL of 0.1 N  $\text{H}_2\text{SO}_4$ .

$$\therefore \text{Normality of the made up solution} = \frac{8.5 \text{ mL} \times 0.1 \text{ N}}{50 \text{ mL}} = 0.017 \text{ N} \quad \dots(c)$$

Thus, reduction in normality,  $(b) - (c) = 0.02 - 0.017 = 0.003 \text{ N}$ .

We know that, carbonate hardness does not consume any alkali mixture, any consumption of the alkali (corresponding to 0.003 N) must be due to the non-carbonate hardness.

Hence, normality of solution w.r.t. non carbonate hardness = 0.003 N

$\therefore$  Non-carbonate hardness (in terms of  $\text{CaCO}_3$  equivalents)

$$= 0.003 \times 50 \times 1000 = 150 \text{ ppm} \quad \dots(d)$$

(iii) Total hardness of the water sample = Carbonate hardness + Non-carbonate hardness

$$= 90 + 150 = 240 \text{ ppm}$$

**Example 7.** A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 ml of water sample on titration with N/50 HCl required 5.0 ml of the acid upto phenolphthalein end point. Few drops of methyl orange were added to the same solution and titration was further continued. The yellow colour of the solution just turned red after the addition of another 11.0 ml of the acid solution. Calculate the type and extent of alkalinity present in the water sample.

[GGSIPU, 1st term, Sept. 2005]

$$\text{Solution. (i) } 100 \text{ mL} \times N_p = 5 \text{ mL} \times \frac{N}{50}$$

$$\therefore P = N_p \times 50 \text{ g/L}$$

$$= 5 \times \frac{N}{50} \times \frac{1}{100} \times 50 = 0.05 \text{ g/L} \quad \dots(1)$$

$$(ii) 100 \text{ mL} \times N_M = (5 + 11) \times \frac{N}{50}$$

$$\Rightarrow N_M = 16 \times \frac{1}{50} \times \frac{1}{100} N$$

$$\Rightarrow M = N_M \times 50 \text{ g/L}$$

$$= 16 \times \frac{1}{50} \times \frac{1}{100} \times 50 = 0.16 \text{ g/L}$$

...(2)

(iii) From (1) and (2),

$$0.05 < \frac{0.16}{2}$$

or

$$P < \frac{M}{2}$$

$\therefore \text{CO}_3^{2-}, \text{HCO}_3^-$  ions make the given water alkaline.

$$(iv) \text{CO}_3^{2-} = 2P = 2 \times 0.05 = 0.1 \text{ g/L} = 0.1 \times 1000 = 100 \text{ ppm.}$$

$$\text{HCO}_3^- = M - 2P = 0.16 - 2 \times 0.05 = 0.06 \text{ g/L} = 60 \text{ ppm.}$$

**Example 8.** 100 mL of a sample of hard water neutralizes 12 mL of 0.12 N HCl using methyl orange as indicator. What kind of hardness is present? Express the hardness in terms of an equivalent of  $\text{CaCO}_3$ ?

**Solution.** We know that methyl orange indicator does not give the value for permanent hardness. Thus, in this question, hardness of water is **temporary**.

Given, Normality of HCl =  $N_1 = 0.12 \text{ N}$

Volume of HCl =  $V_1 = 12 \text{ mL}$

Volume of hard water =  $V_2 = 100 \text{ mL}$

Let, Normality of hard water =  $N_2$

Applying the Normality equation,

$$N_1 V_1 = N_2 V_2$$

$$\Rightarrow 0.12 \text{ N} \times 12 \text{ mL} = N_2 \times 100 \text{ mL}$$

$$\Rightarrow N_2 = \frac{0.12 \times 12}{100} \text{ N}$$

As equivalent weight of  $\text{CaCO}_3 = 50$

$\therefore$  Strength of hardness (in terms of equivalent of  $\text{CaCO}_3$ ) =  $N_2 \times 50 \text{ g/L}$

$$\Rightarrow \text{Strength} = \frac{0.12 \times 12}{100} \times 50 \text{ g/L} = 0.72 \text{ g/L}$$

$$\Rightarrow \text{Temporary hardness} = 0.72 \text{ g/L} \\ = 0.72 \times 1000 \text{ mg/L} = 720 \text{ mg/L}$$

or Temporary hardness = 720 ppm.

### Review Questions

1. A sample of water was found to contain the following:

$\text{Ca}^{2+} = 40 \text{ mg/L}$ ,  $\text{Mg}^{2+} = 24 \text{ mg/L}$ ,  $\text{Na}^+ = 9.2 \text{ mg/L}$  and  $\text{HCO}_3^- = 183 \text{ mg/L}$ ,

$\text{SO}_4^{2-} = 57.5 \text{ mg/L}$ ,  $\text{Cl}^- = 7.0 \text{ mg/L}$ . Express these in terms of equivalents of  $\text{CaCO}_3$ .



[Ans.

Constituent	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>
CaCO <sub>3</sub> equivalent (ppm)	99	98.5	20	150	58	9.5
	= 217.5 ppm			= 217.5 ppm]		

2. 200 mL of a sample required 20 mL of N/50 HCl using methyl orange as indicator. Another 200 mL of the same sample required 8 mL of N/50 HCl using phenolphthalein as indicator. Express the alkalities in terms of mg of CaCO<sub>3</sub> per litre.

[Ans. CO<sub>3</sub><sup>2-</sup> = 80 mg/L ; HCO<sub>3</sub><sup>-</sup> = 20 mg/L]

3. 100 mL of a sample of water required 15 mL of 0.01 M EDTA for titration using EBT as indicator. In another experiment, 100 mL of the same sample was boiled to remove the carbonate hardness, the precipitate was removed and the cold solution required 8.0 mL of 0.01 M EDTA using EBT as indicator. Calculate (i) Carbonate hardness, (ii) Permanent or non-carbonate hardness, and (iii) Total hardness in ppm of CaCO<sub>3</sub>.

[Ans. (i) 70 ppm, (ii) 80 ppm and (iii) 150 ppm]

4. Using the data given in Q. 1 above, express the results in terms of salts.

**Solution.** Equivalent amounts of cations and anions are paired as follows :

First the HCO<sub>3</sub><sup>-</sup> is paired with Ca<sup>2+</sup> to give Ca alkalinity. ∴ Ca alkalinity = 99 ppm,

Any alkalinity left over (150 - 99 = 51 ppm) is paired with Mg<sup>2+</sup>. ∴ Mg alkalinity = 51 ppm. The remaining HCO<sub>3</sub><sup>-</sup>, if any, is paired with Na<sup>+</sup>. Here, it is zero ppm.

As salts of Ca<sup>2+</sup> and Mg<sup>2+</sup> contribute in hardness.

∴ Total hardness = 99 + 98.5 = 197.5 ppm

Given HCO<sub>3</sub><sup>-</sup> = 150 ppm so carbonate hardness = 150 ppm

From above 2 results, non carbonate hardness = 197.5 - 150 = 47.5 ppm. From 98.5 ppm of Mg<sup>2+</sup> ; 51 ppm of Mg<sup>2+</sup> has already been combined with HCO<sub>3</sub><sup>-</sup> so there is a balance of 47.5 ppm. This is combined with the non-carbonate hardness.

Thus, Mg non-carbonate hardness = 47.5 ppm

In this case, only SO<sub>4</sub><sup>2-</sup> ions are there, contributing towards non-carbonate hardness.

Thus, MgSO<sub>4</sub> = 47.5 ppm

Always, non-carbonate hardness is first paired with Mg<sup>2+</sup> and then remaining is paired with Ca<sup>2+</sup>.

In this case, Ca non carbonate hardness = 0 ppm.

We had total 58 ppm SO<sub>4</sub><sup>2-</sup>. Out of these, 47.5 ppm is in MgSO<sub>4</sub> form so remaining 10.5 ppm of SO<sub>4</sub><sup>2-</sup> and 9.5 ppm of Cl<sup>-</sup> will combined with 20 ppm of Na<sup>+</sup>.

Thus, the ionic analysis can be expressed in the form of salts as :

Ca(HCO<sub>3</sub>)<sub>2</sub> = 99 ppm ; MgSO<sub>4</sub> = 47.5 ppm ;

Mg(HCO<sub>3</sub>)<sub>2</sub> = 51 ppm ; Na<sub>2</sub>SO<sub>4</sub> = 10.5 ppm ; NaCl = 9.5 ppm.

## 8 BOILER FEED WATER (WATER FOR STEAM GENERATION)

A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. In the boiler furnace, the chemical energy in the fuel is converted into heat, and it is the function of the boiler to transfer this heat to the contained water in the most efficient manner. The boiler should also be designed

to generate high quality steam for plant use. A boiler must be designed to absorb the maximum amount of heat released in the process of combustion. This heat is transferred to the boiler water through radiation, conduction and convection.

**Steam utilization.** Steam is generated for the following plant uses :

- (i) Turbine drive for electric generating equipment, blowers and pumps,
- (ii) Heating and air conditioning for equipment and comfort,
- (iii) Process for direct contact with products, direct contact sterilization and noncontact for processing temperatures.

Water is mainly used in boilers for the generation of steam (for industries and power houses). For such water all the impurities are not necessarily eliminated, and only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits.

*A boiler-feed water should correspond with the following composition :*

- (i) Its hardness should be below 0.2 ppm.,
- (ii) Its caustic alkalinity (due to  $\text{OH}^-$ ) should lie in between 0.15 and 0.45 ppm.
- (iii) Its soda alkalinity (due to  $\text{Na}_2\text{CO}_3$ ) should be 0.45 – 1 ppm.

Excess of impurities, if present, in boiler feed water generally cause the following problems :

Scale and sludge formation, corrosion, priming and foaming, caustic embrittlement.

### Essential Requirements of Boiler Feed Water

Boiler feed water should be free from

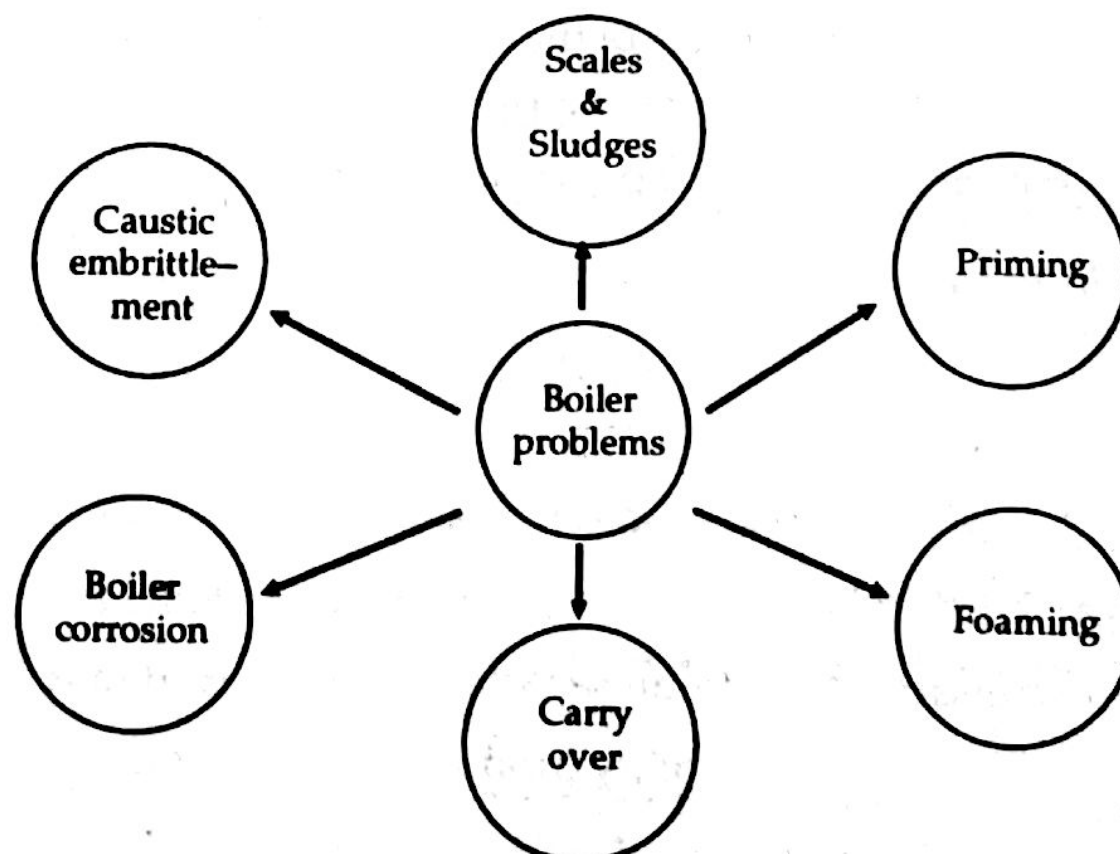
1. **Hardness** causing and scale forming constituents like salts of calcium and magnesium. This is because scale formation would result in wastage of fuel, lowering of boiler safety, decrease in efficiency and danger of explosion.

2. **Caustic alkali** to avoid caustic embrittlement.

3. **Dissolved gases** like  $\text{O}_2$ ,  $\text{CO}_2$  etc. in order to prevent boiler corrosion, and

4. **Turbidity, oil** etc. to reduce the tendency for priming and foaming.

## 9 BOILER PROBLEMS



Summary of Boiler problems



### 9.1 Sludge and Scale Formation in Boilers

In a boiler, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed are soft loose and slimy, these are known as *sludges*; while if the precipitate is hard and adhering on the inner walls, it is called as *scale*.

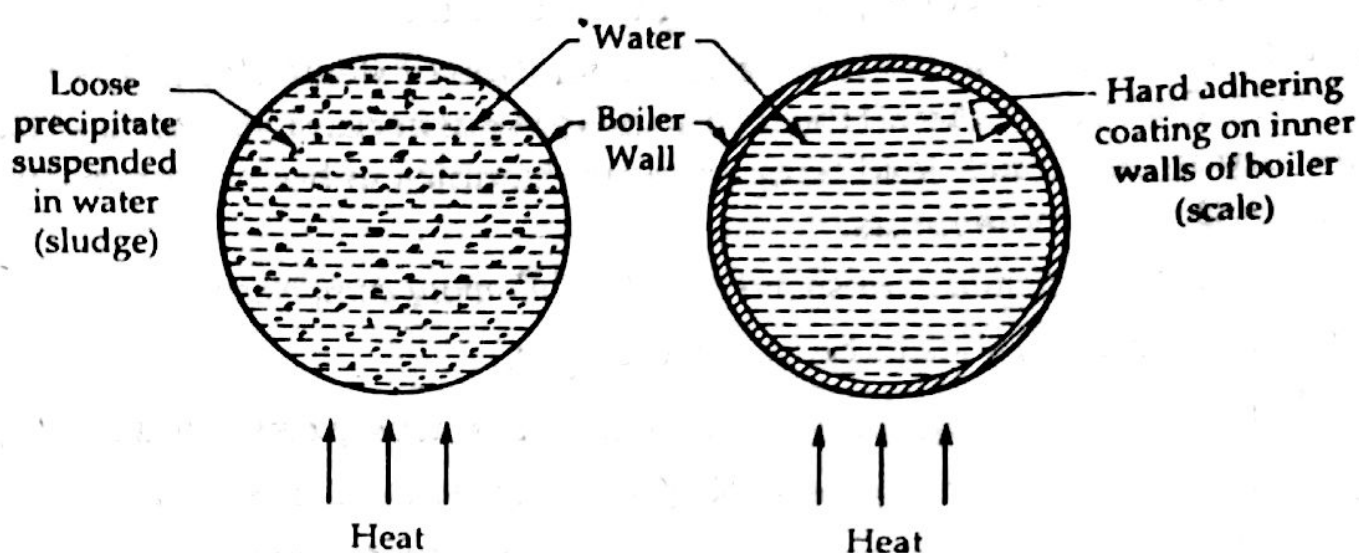
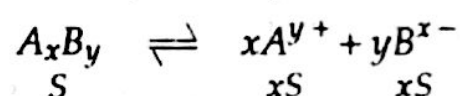


Fig. 4. Sludge and scale formation in boilers.

Note : In general, for an electrolyte,  $A_xB_y$ , which ionises as :



The solubility product ( $K_{SP}$ ) is given by :  $K_{SP} = [A^{y+}]^x [B^{x-}]^y$

where  $[A^{y+}]$  and  $[B^{x-}]$  are the ionic concentrations in a saturated solution. Thus, solubility product of an electrolyte may be defined as "the maximum product of the concentrations of its constituent ions (expressed in moles per Litre) in its solution, when each ionic concentration term being raised to the no. of times the ion occurs in the equation representing the solution of 1 molecule of the electrolyte."

Let  $S$  mole/Litre be the solubility of the electrolyte, then concentration,

$$[A^{y+}] = x S \text{ mol/L and } [B^{x-}] = y \cdot S \text{ mole/L}$$

$$\therefore K_{SP} = [A^{y+}]^x [B^{x-}]^y = [xS]^x [y.S]^y = x^x \cdot y^y \cdot S^{x+y}$$

For example, in case of  $BaCl_2 \rightleftharpoons Ba^{2+} + 2 Cl^-$  ;  $x = 1, y = 2$ .

$$K_{SP} = 1^1 \cdot 2^2 \cdot S^{1+2} = 4 S^3$$

Cases :

1. If  $K_{SP} = [A^{y+}]^x [B^{x-}]^y \Rightarrow$  solution is just saturated
2. If  $K_{SP} > [A^{y+}]^x [B^{x-}]^y$  or solubility product > ionic product  
 $\Rightarrow$  Solution is unsaturated and more salt can be dissolved in it.
3. If  $K_{SP} < [A^{y+}]^x [B^{x-}]^y$  or solubility product < ionic product  
 $\Rightarrow$  Solid  $A_xB_y$  will precipitate out.

**SLUDGE**

Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solubilities in hot water than in cold water, e.g.,  $\text{MgCO}_3$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgSO}_4$  etc. They are formed at comparatively colder portions of the boiler and get collected at places where the flow rate is slow, they can be easily removed (scrapped off) with a wire brush.

If sludges are formed along-with scales, then former gets entrapped in the latter and both get deposited as scales.

**Disadvantages of sludge formation**

- (i) Sludges are poor conductors of heat, so they tend to waste a portion of heat generated and thus decrease the efficiency of boiler.
- (ii) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

**Prevention of sludge formation**

- (i) By using softened water
- (ii) By frequently 'blow-down operation', (i.e., partial removal of concentrated water through a tap at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high.)

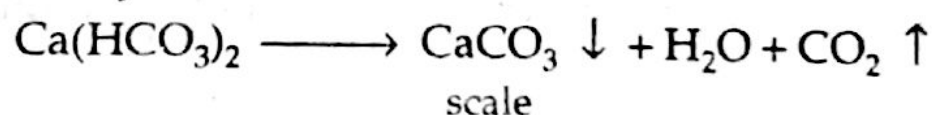
**SCALES**

Scales are hard deposits firmly sticking to the inner surfaces of the boiler.

They are difficult to remove, even with the help of hammer and chisel, and are the main source of boiler troubles.

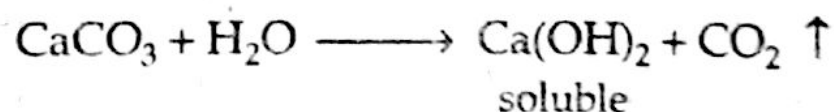
*Scales may be formed inside the boiler due to :*

- (i) *Decomposition of calcium bicarbonate*



However, scale composed chiefly of calcium carbonate is soft and is the *main cause of scale formation in low-pressure boilers*.

But in high-pressure boilers,  $\text{CaCO}_3$  is soluble due to the formation of  $\text{Ca}(\text{OH})_2$



- (ii) *Deposition of calcium sulphate*

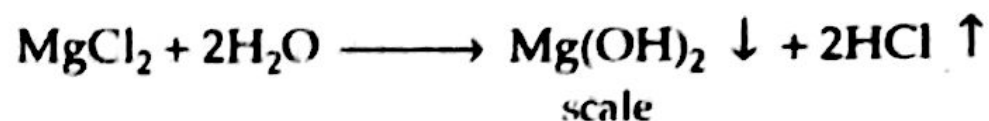
The solubility of  $\text{CaSO}_4$  in water decreases with increase in temperature.  $\text{CaSO}_4$  is soluble in cold water, but almost completely insoluble in super-heated water. [It may be due to increased ionization at high temperature so  $k_{sp} < k_{\text{ionic prod.}}$  and less availability of water molecules for solvation at high temperature.

Consequently,  $\text{CaSO}_4$  gets precipitated as hard scale on the hotter parts, of the boiler. *This type of scale causes troubles mainly in high-pressure boilers.* Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.



(iii) *Hydrolysis of magnesium salts*

Dissolved magnesium salts get hydrolysed (at prevailing high temperature inside the boiler) forming magnesium hydroxide precipitate, which forms a soft type of scale, e.g.

(iv) *Presence of silica*

Even if a small quantity of  $\text{SiO}_2$  is present, it may deposit as calcium silicate ( $\text{CaSiO}_3$ ) and/or magnesium silicate ( $\text{MgSiO}_3$ ). These deposits adhere very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

✱ **Explain the reasons for the depositions of some substances as scales.**

**Ans.** *Explanation due to hall*, when a steam bubble is formed on a heated surface, the salts contained in the solution get deposited along the over-heated peripheral region of the bubble. When the bubble leaves the surface or bursts, water coming into contact with the hot metal surface is super-heated ; and being saturated with  $\text{CaSO}_4$ , deposits the same as scale. Deposition of scale proceeds as evaporation continues.

*Explanation due to partridge*, scale is produced when steam bubbles form so rapidly in a given place that the solid deposited under one is not completely washed away by water before the formation of a subsequent bubble.

**Disadvantages of Scale formation**

(i) *Wastage of fuel*. Scales have a poor thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or over-heating is done and this causes increase in fuel consumption.

The wastage of fuel being dependent on the thickness and the nature of scale :

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(ii) *Lowering of boiler safety*. Due to scale formation, over-heating of boiler is done in order to maintain a steady supply of steam. It makes the boiler material softer and weaker. This causes distortion of boiler tube and also makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.

(iii) *Decrease in efficiency*. Deposition of scales in the valves and condensers of the boiler, choke them partially. This results in decrease in efficiency of the boiler.

(iv) *Danger of explosion*. When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in development of sudden high-pressure which may cause explosion of the boiler.

### Removal of Scales

Scales are removed by mechanical methods (i - iii) and/or by chemical methods (iv).

- (i) If the scales are loosely adhering, it can be removed with the help of scraper or piece of wood or wire brush,
- (ii) If the scales are brittle, it can be removed by giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water),
- (iii) If the scales are loosely adhering, they can also be removed by frequent blow-down operation. Blow-down operation is partial removal of hard water through a 'tap' at the bottom of the boiler, when extent of hardness in the boiler becomes alarmingly high. 'Make-up' water is addition of fresh softened water to boiler after blow down operation.
- (iv) If the scales are adherent and hard, they can be removed by dissolving them by adding chemicals e.g.,  $\text{CaCO}_3$  scales can be dissolved by using 5 - 10% HCl. Calcium sulphate scales can be removed by adding EDTA, since the Ca - EDTA complex is highly soluble in water.

The essential differences between sludges and scales are summarized in Table 5 :

**Table 5. Differences between Sludges and Scales**

S.No.	Sludges	Scales
1.	Sludges are soft, loose and slimy precipitate.	Scales are hard deposits.
2.	They are non-adherent deposits and can be easily removed.	They stick very firmly to the inner surface of boiler and are very difficult to remove.
3.	Formed by substances like $\text{CaCl}_2$ , $\text{MgCl}_2$ , $\text{MgSO}_4$ , $\text{MgCO}_3$ etc.	Formed by substance like $\text{CaSO}_4$ , $\text{Mg(OH)}_2$ etc.
4.	Formed at comparatively colder portions of the boiler.	Formed generally at heated portions of the boiler.
5.	They decrease the efficiency of boiler but are less dangerous.	Decrease the efficiency of boiler and chances of explosions are also there.
6.	Can be removed by blow-down operation.	Cannot be removed by blow-down operation.

### 9.2 Priming and Foaming

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along-with the steam. This process of 'wet-steam' formation, is called *priming*.

**Priming** refers to the propulsion of water into the steam drum by extremely rapid, almost explosive boiling of the water at the heating surfaces.

The moisture contamination in the steam is expressed in percentage by weight of steam.

For example, if steam contains 0.2% moisture, its steam quality will be reported as  $100 - 0.2 = 99.8\%$ .

*Priming is caused by :*

- (i) the presence of considerable quantities of dissolved solids (mainly due to suspended impurities and due to dissolved impurities in water).



- (ii) Steam velocities high enough to carry droplets of water into the steam pipe ;
- (iii) Sudden boiling ;
- (iv) Faulty design of boiler.

*Priming can be avoided by :*

- (i) controlling rapid change in steaming velocities,
- (ii) the proper design of boilers (maintaining low water levels in boilers),
- (iii) ensuring efficient softening and
- (iv) filtration of the boiler-water carried over to the boiler.
- (v) by blowing off sludge or scales from time to time.

**Foaming** is the formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily. *Foaming is caused by* the presence of an oil and alkalis in boiler-feed water. Actually oils and alkalis react to form soaps which greatly lowers the surface tension of water and thus increase the foaming tendency of the liquid.

With respect to foaming, water can be of following grades :

- (i) *Foaming water*. It is that water which produces foam even in two days. if blowing off operation is not done.
- (ii) *Semi-Foaming water*. It is that water which does not produce any foam in locomotive boilers for two days.
- (iii) *Non-Foaming water*. It is that water which does not produce any foam in locomotive boilers for one week.

*Foaming can be avoided by :* (i) the addition of anti-foaming agents, which act by counteracting the reduction in surface tension. For example addition of castor oil (which spreads on the surface of water and therefore) neutralises the surface tension reduction. (ii) The removal of foaming agent (oil) from boiler water.

Traces of oils are generally introduced in boiler feed water through the lubricating materials used for pumps etc. Oils can be removed by the addition of aluminium compounds, like *sodium aluminate* and *aluminium sulphate* which are hydrolysed to form aluminium hydroxide flocks which entrap oil drops. The flocks of  $\text{Al}(\text{OH})_3$  containing oil droplets are removed by filtration through anthrafil filter bed.

### 9.3 Carry Over

The phenomenon of carrying of water along with impurities by steam is called "carry over". This is mainly due to priming and foaming.

*Priming and foaming*, usually occur together.

They are objectionable because :

- (i) dissolved salts or suspended solids in boiler water are carried by the wet steam to superheater and turbine blades, where they get deposited as water evaporates. This deposit decreases the efficiency of boiler.
- (ii) dissolved salts may enter the parts of other machinery, thereby decreasing their life ;
- (iii) The maintenance of the boiler pressure becomes difficult because of improper judgement of actual height of water column.

### 9.4 Boiler Corrosion

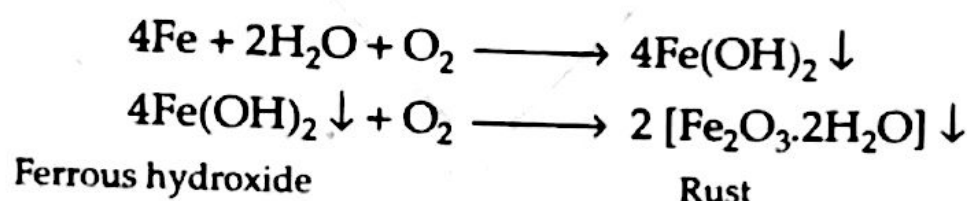
Boiler corrosion is "decay" or "disintegration" of boiler body material either due to chemical or electrochemical reaction with its environment.

The disadvantages of corrosion are :

- (i) Shortening of boiler life,
- (ii) leakages of the joints and rivets ;
- (iii) increased cost of repairs and maintenance.

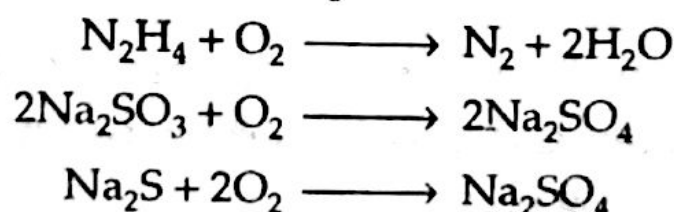
Corrosion in boilers is due to the following reasons :

(1) **Dissolved oxygen.** This is the most usual corrosion causing factor. In boilers, oxygen is introduced through the raw water supply. Water usually contains about 8 ppm of dissolved oxygen at room temp. As the water is heated, the dissolved oxygen is set free and the boiler starts corroding. Dissolved oxygen reacts with the iron of boiler in presence of water and under prevailing high temp. to form ferric oxide (rust).



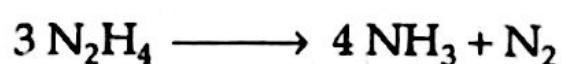
*Removal of dissolved oxygen :*

(i) By adding hydrazine or sodium sulphite or sodium sulphide. Thus :



Hydrazine is an ideal chemical for the removal of dissolved oxygen. It reacts with oxygen, forming nitrogen and water. Nitrogen is harmless. Consequently, hydrazine removes oxygen without increasing the conc. of dissolved solids/salts.

- (a) Pure hydrazine is not used in water treatment because it is an explosive inflammable liquid so 40% Aqueous solution of hydrazine is used which is quite safe.
- (b) Excess hydrazine must not be used because excess of it decomposes to give  $\text{NH}_3$ , which causes corrosion of some alloys like brass etc. used in condensor tubes.



On the other hand, if sodium sulphite or sodium sulphide is used, the sodium sulphate is formed. Under high pressure it decomposes giving  $\text{SO}_2$ . The  $\text{SO}_2$  enters the steam pipes and appears as corrosive sulphurous acid ( $\text{H}_2\text{SO}_3$ ) in steam condensate. So as a rule a very low concentration of 5-10 ppm of  $\text{Na}_2\text{SO}_3$  in the boiler is maintained, rather adding it intermittently.

(ii) *By mechanical deaeration.* This process consists of spraying water over preheated perforated plates stacked in a degasifier. Removal of dissolved  $\text{O}_2$  is ensured by applying high temperature and vacuum.



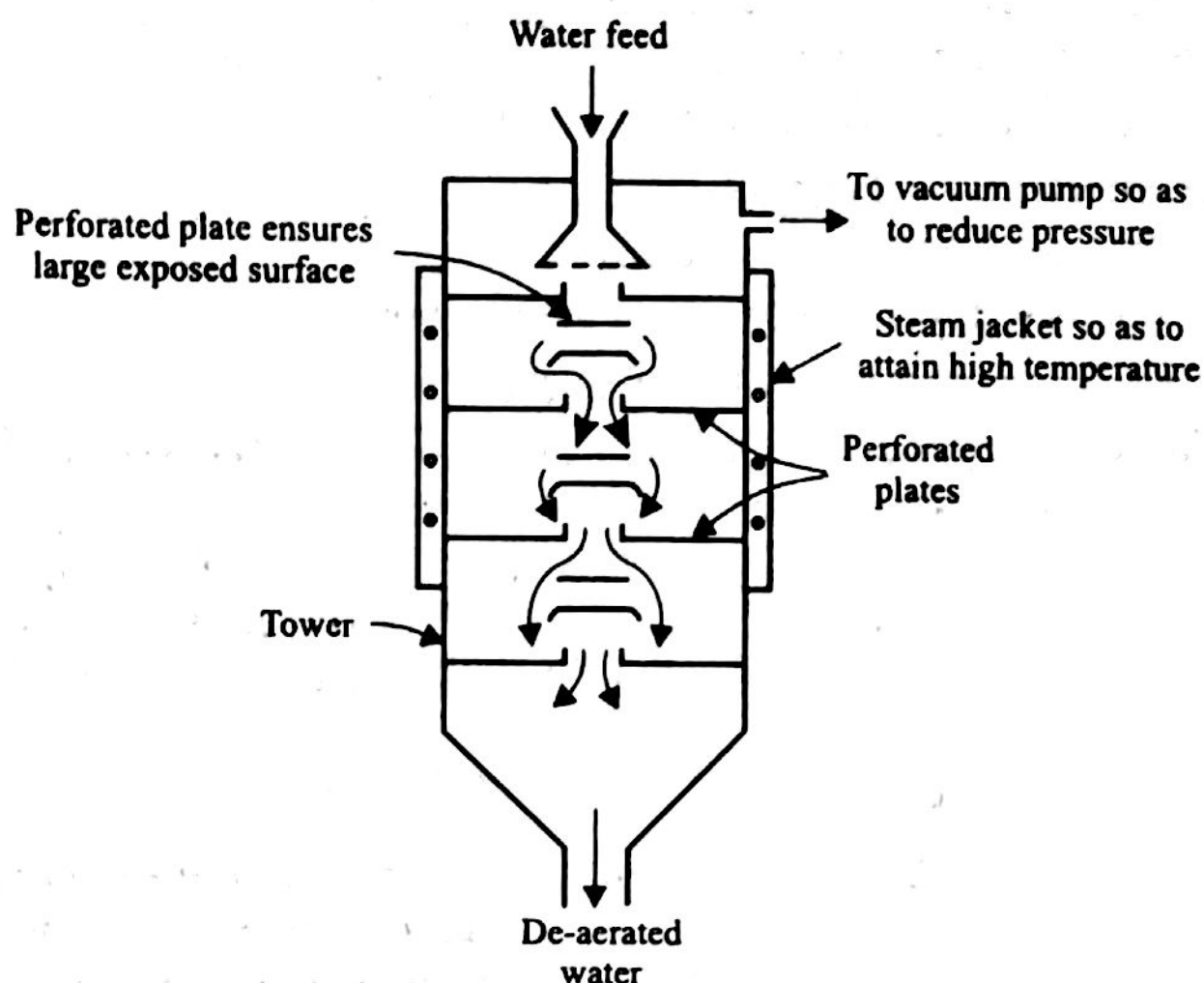
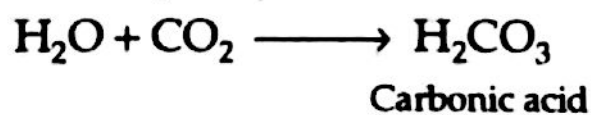


Fig. 5. Mechanical de-aeration of water.

(2) **Carbon dioxide.** There are two sources of  $\text{CO}_2$  in boiler water, viz. dissolved  $\text{CO}_2$  in raw water and  $\text{CO}_2$  formed by decomposition of bicarbonates in  $\text{H}_2\text{O}$  according to the equation :



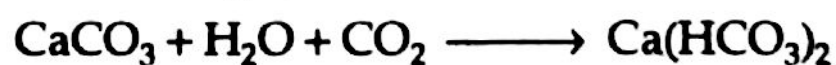
Carbon dioxide in presence of water forms carbonic acid which has a corrosive effect on the boiler material like any other acid.



$\text{CO}_2$  can be removed by :

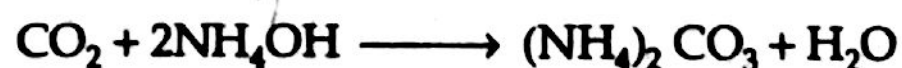
(i) mechanical de-aeration along with  $\text{O}_2$ .

(ii) filtering water through lime-stone

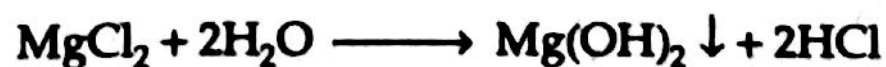


But this method increases hardness

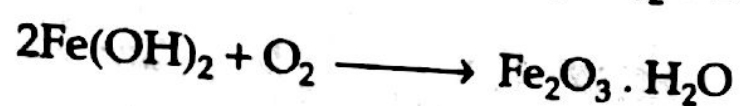
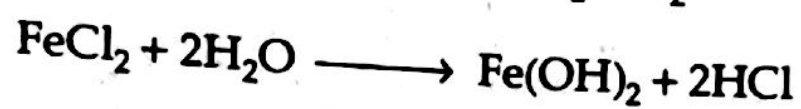
(iii) addition of appropriate quantity of ammonium hydroxide



(3) **Mineral acids.** Magnesium chloride, if present in boiler feed water, can undergo hydrolysis producing  $\text{HCl}$



The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust in the following way :



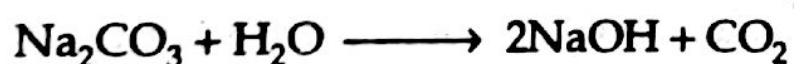
Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Consequently, presence of even a small amount of  $\text{MgCl}_2$  cause corrosion of iron to a large extent.

As the boiler water is generally alkaline and hence the acid is usually neutralized. In case, the amount of acid is more, calculated quantity of alkali is added from outside to neutralize the acid for preventing this corrosion.

### 9.5 Caustic Embrittlement

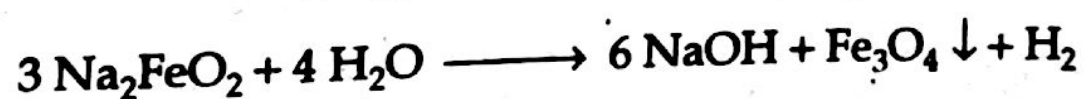
Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

During softening by lime-soda process, it is likely that some residual  $\text{Na}_2\text{CO}_3$  is still present in the softened water. In high pressure boilers  $\text{Na}_2\text{CO}_3$  decomposes to give sodium hydroxide and  $\text{CO}_2$ , and sodium hydroxide thus produced makes the boiler water "caustic".



This caustic water flows into the minute hair-cracks, present in the inner side of boiler, by capillary action. On evaporation of water the dissolved caustic soda concentration increases progressively which attacks the surrounding area, thereby dissolving iron of boiler as Sodium ferroate ( $\text{Na}_2\text{FeO}_2$ ).

From its place of formation, sodium ferroate decomposes a short distance away as per the following equation :



Further dissolution of iron takes place because of

- (i) The precipitation of  $\text{Fe}_3\text{O}_4$ , and
- (ii) The regeneration of NaOH.

This causes embrittlement of boiler walls more particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.

Mechanistically embrittlement arises due to the setting up of a concentration cell.



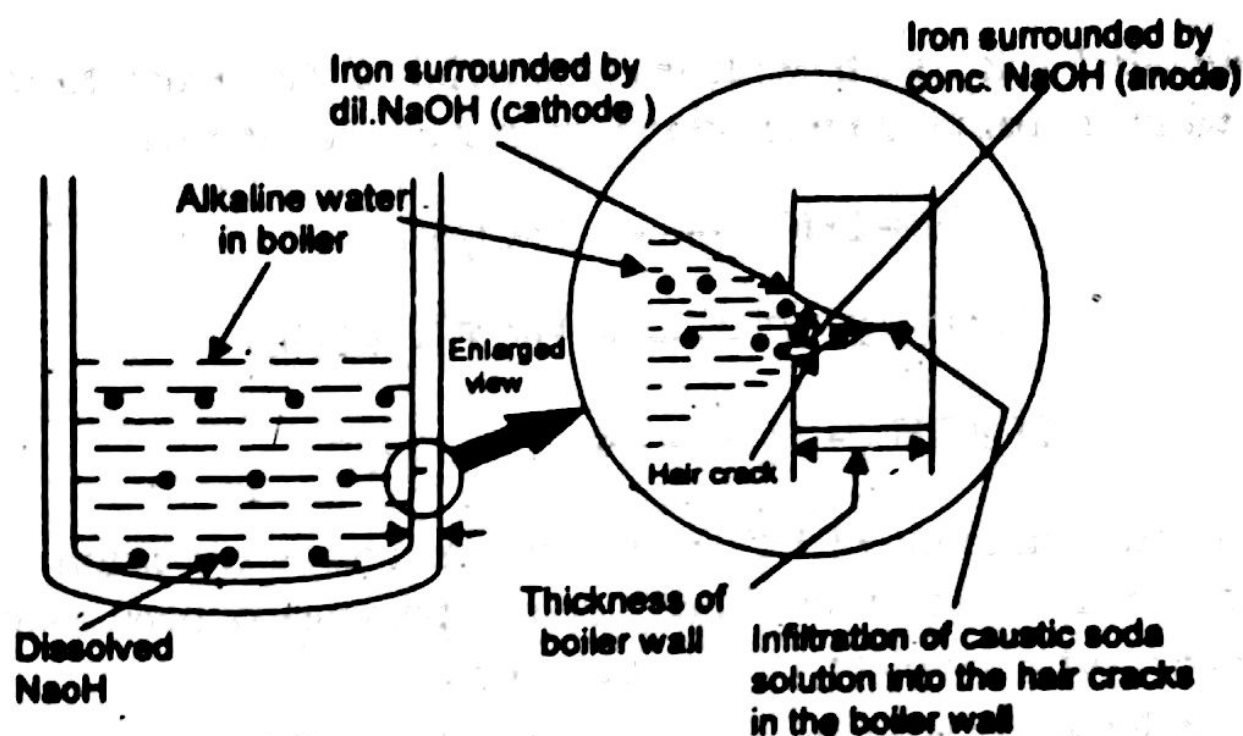


Fig. 6. The cause of caustic embrittlement is setting up of a concentration cell.

With the iron surrounded by *dil. NaOH* acting as the *Cathode*, while the iron surrounded by *conc. NaOH* acting as the *anode*.

The iron in the anodic part gets dissolved or corroded.

*Caustic embrittlement can be prevented :*

- (i) by using sodium phosphate as softening reagent, instead of sodium carbonate in external treatment of boiler water.
- (ii) by adding tannin or lignin to boiler water which blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution into these areas.
- (iii) by adding sodium sulphate to boiler water :

$\text{Na}_2\text{SO}_4$  also blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these. It has been observed that caustic cracking can be prevented, if  $\text{Na}_2\text{SO}_4$  is added to boiler water so that the ratio :

$\frac{[\text{Na}_2\text{SO}_4 \text{ conc.}]}{[\text{NaOH conc.}]}$  is kept as 1 : 1, 2 : 1 and 3 : 1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

☛ Discuss reasons of removal of silica from water. How it can be removed ?

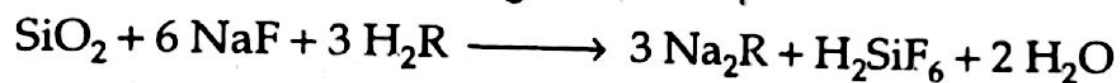
**Ans. Purpose of silica removal.** Silica is not desirable in boiler feed water, because it forms troublesome scales in medium (upto  $56.24 \times 10^4 \text{ kg/m}^2$  or 800 psi) and high pressure ( $> 56.24 \times 10^4 \text{ kg/m}^2$ ) boilers. However, small quantities of silica are not objectionable in low pressure boilers, (upto  $1.76 \times 10^4 \text{ kg/m}^2$  or 250 psi).

**Scales which may form in the presence of silica.** The silica may form silica scale itself, calcium silicate scale or sodium aluminium silicate scale. These scales formation have the disadvantages associated with them like fuel wastage, chances of explosion etc. during boiler operations. So, it is must to remove silica.

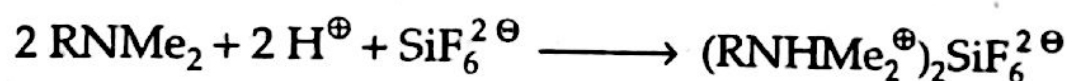
Following methods can be used for the removal of silica from the boiler feed water :

- (i) By the addition of ferrous sulphate ( $\text{Fe}_2(\text{SO}_4)_3$ ) or sodium aluminate as coagulants. They act as  $\text{Fe}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  which trap finely suspended and colloidal impurities including silica and oil.
- (ii) By pre-treatment with magnesia ( $\text{MgO}$ ) or dolomitic lime, after the removal of temporary hardness. Magnesia acts as magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) which traps silica by adsorption phenomenon.
- (iii) By conversion of  $\text{SiO}_2$  to  $\text{H}_2\text{SiF}_6$  using  $\text{HF}$  and then removal of  $\text{H}_2\text{SiF}_6$  using anion exchangers.

Silicic acid ( $\text{H}_2\text{SiO}_3$ ) is very feebly ionized and is not removed by passing it over weakly basic anion exchanger. Thus, silica ( $\text{SiO}_2$ ) is first converted to fluoro silicic acid ( $\text{H}_2\text{SiF}_6$ ) by adding sodium fluoride and then passing through hydrogen cation exchanger.



Fluorosilicic acid ( $\text{H}_2\text{SiF}_6$ ) is strongly ionized and can be removed by using anion exchangers :



This process is costly.

☛ **Why the silica, oil and dissolved gases should not be present in the boiler feed water ?**

Ans. (i) In low pressure boilers (upto 250 psi), small quantities of silica are not objectionable.

But in medium (upto 800 psi) and high (> 800 psi) pressure boilers, silica forms troublesome calcium silicate scale, silica scale or sodium aluminium silicate scale. That's why silica is not desirable in boiler water.

(ii) Oil is not desirable in boiler water because even small quantities of oils form heat-insulating films on the boiler material. The oil may be hydrolyzed to give fatty acids, which may bring in problems of corrosion.

(iii) Dissolved gases like  $\text{O}_2$ ,  $\text{H}_2\text{S}$  and  $\text{SO}_2$  are not desirable in boiler water because oxygen promotes corrosion and  $\text{H}_2\text{S}$  and  $\text{SO}_2$  gases attack the boiler material.

## 10 WATER SOFTENING

The process whereby we remove or reduce the hardness of water, irrespective of whether it is temporary or permanent is termed as 'softening' of water. It is very essential process since hard water is unsuitable for domestic as well as industrial use. One of the most important applications of water is in steam production for the generation of electricity. For this water need to be fed to industrial boilers. We just cannot feed any water into the industrial boilers because it has been identified that hard water creates large number of problems like scale and sludge formation, priming and foaming etc.



The hardness causing salts can be removed from water by following two ways :

(a) External treatment, and (b) Internal treatment.

The *External treatment* of water is carried out before its entry into the boiler. This treatment prevents boiler problems. It can be done by lime-soda, zeolite or ion-exchange processes. All are preventive methods.

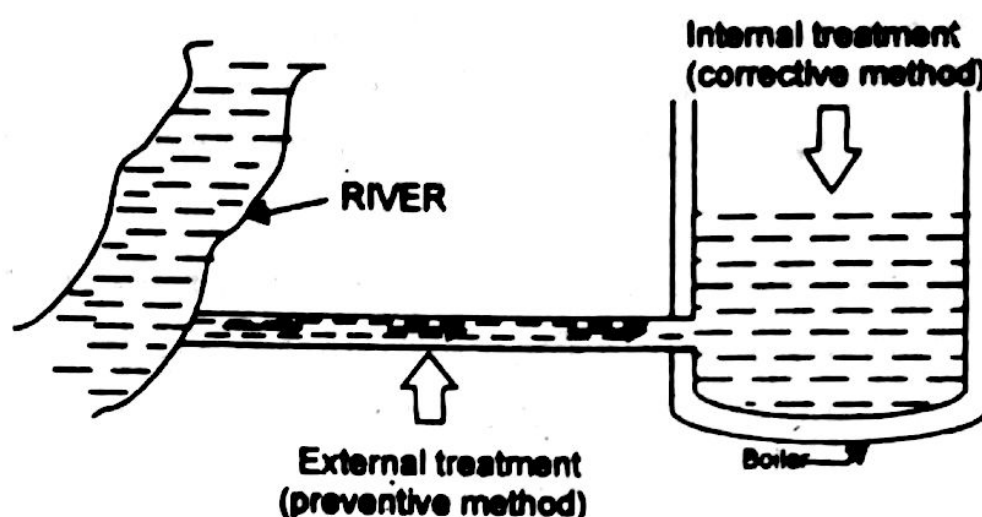
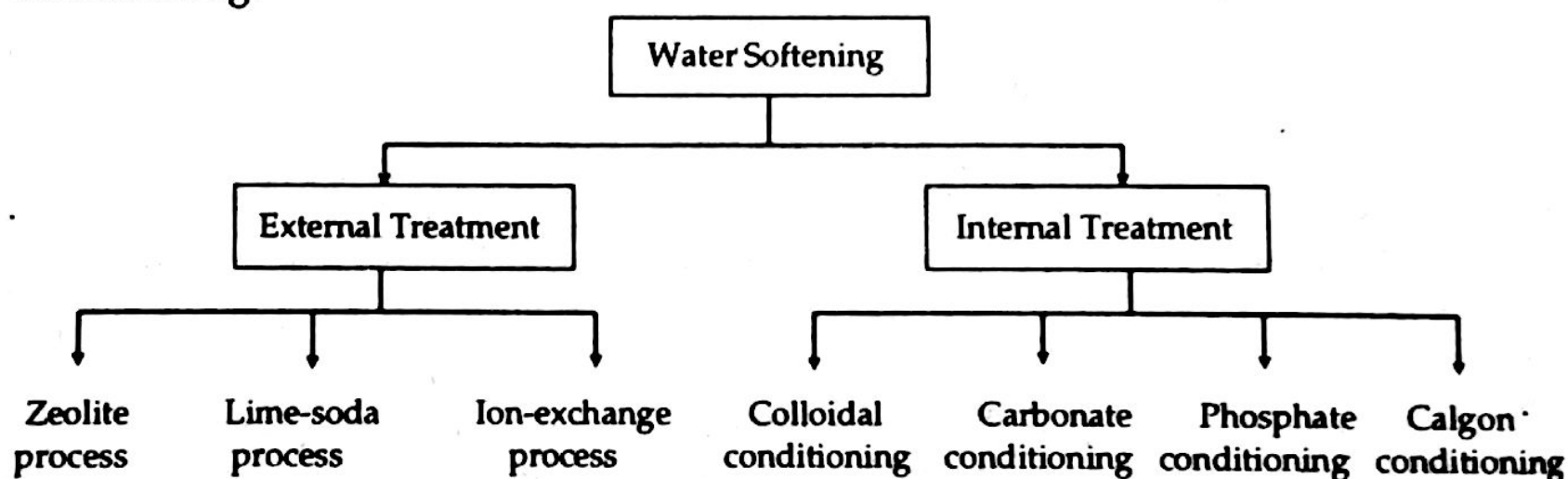


Fig. 7. Illustration of types of water treatment methods and there point of application.

In contrast, the *Internal treatment* of boiler feed water refers to the conditioning of water in the boiler itself by the addition of chemicals. This is essentially a corrective method to remove those salts which are not completely removed by external treatment of water softening. The following conditioning methods are used in the Internal treatment : Colloidal, Phosphate, Calgon and Carbonate conditioning.



The essential difference between the External treatment and Internal treatment methods are summarized in Table 6.

Table 6. Differences between Internal and External treatment methods

S.No.	Internal treatment (Corrective methods)	External treatment (Preventive methods)
1.	It is carried out in the boiler itself	It is carried out outside the boiler, before water enters the boiler.
2.	It is required in low-pressure boilers	It is required in high-pressure boilers.
3.	It is a corrective method	It is a preventive method.
4.	It includes colloidal conditioning, carbonate conditioning, Phosphate conditioning, Calgon conditioning etc.	It includes zeolite process, lime-soda process and ion-exchange process.

## 11 EXTERNAL TREATMENT

It can be done by the following methods :

(i) Lime-soda process, (ii) Zeolite process, and (iii) Ion-exchange process

These important methods by which hard water is commonly softened are discussed below :

### 11.1 Lime-Soda Process

The basic principle of this process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates which may be removed by settling and filtration. For this purpose, a suspension of milk of lime,  $\text{Ca(OH)}_2$ , together with a calculated amount of sodium carbonate,  $\text{Na}_2\text{CO}_3$  (soda) is added in requisite amount. Proper mixing of the chemicals and water is carried out. Calcium carbonate,  $\text{CaCO}_3$ ; magnesium hydroxide,  $\text{Mg(OH)}_2$ ; ferric hydroxide,  $\text{Fe(OH)}_3$  and aluminium hydroxide,  $\text{Al(OH)}_3$  so precipitated are filtered off.

The chemical reactions taking place during lime-soda treatment are slow. Thus for the efficient use of lime and soda

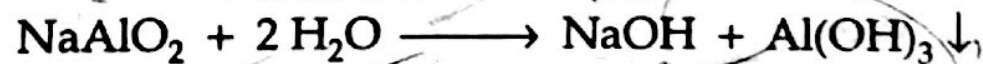
- (i) Proper time for the completion of reactions is given,
- (ii) Thorough mixing of the chemicals and water is carried out,
- (iii) Reaction rates are accelerated by heating as is done in hot lime-soda process.

At room temperature, the precipitates formed are very fine. They do not settle down easily and cause difficulty in filtration. The fine precipitates of  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$  eventually result in "after deposition", later in the pipes and boiler tubes, producing scales. These in turn

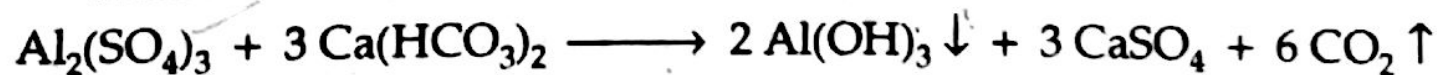
- (a) cause their corrosion,
- (b) clog tubes and valves, and
- (c) decrease the effective diameters of pipes.

These drawbacks partly offset the purpose of water softening.

However, If small amount of coagulants like Alum [ $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ ]; Aluminium sulphate [ $\text{Al}_2(\text{SO}_4)_3$ ] or Sodium aluminate [ $\text{NaAlO}_2$ ] are added, they hydrolyse to precipitate of aluminium hydroxide which entraps the fine precipitate of  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$ . Thus coagulant helps in the formation of coarse precipitates.



Sodium aluminate



Aluminium sulphate      Calcium bicarbonate

There are a number of variations of the lime-soda process :

Like Batch or continuous ; Cold or hot lime soda processes which are briefly described below :

#### (I) Cold Lime Soda Process

In these processes water is treated with lime and soda at room temperature in the presence of coagulant.

There are four types of cold lime soda softeners which work either in batch process or in continuous process. These are briefly discussed on next page :



(a) *The intermittent type (Batch process) Cold Lime-Soda Softener.* It consists of a pair of tanks which are used in turn for softening water. Each tank is equipped with a mechanical stirrer, inlets (for raw water and chemicals) and outlets (for soft water and sludge), see Fig. 8. Raw water and calculated quantities of the chemicals are passed simultaneously into the tank from the opposite sides and the stirring is started with

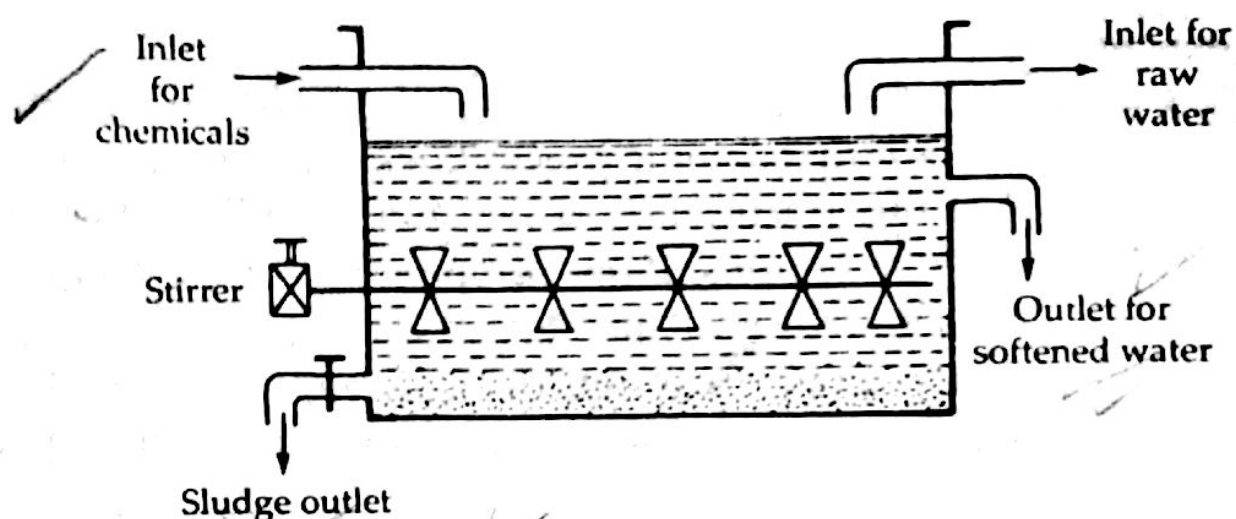


Fig. 8. Intermittent Cold Lime-Soda Softener.

the help of stirrer. For accelerating the process, some sludge (from a previous operation) is also added which acts as nucleus for the fresh precipitation. Reaction is complete by the time tank fills up, and thus stirring is stopped. The sludge (ppt.) formed is allowed to settle down, and is then removed from the tank through the sludge outlet. The softened water is taken out through a floating pipe and sent to the filtering unit. By this batch process, continuous supply of softened water can be ensured by using a pair of tanks planned for alternate cycles of reaction and settling.

(b) *Continuous cold lime-soda softeners. (i) The conventional type.* In this process, raw water and requisite amount of lime, soda and coagulants are fed at room temperature from the top into an inner chamber of vertical circular chamber fitted with a paddle stirrer (see Fig. 9). Vigorous stirring ensures continuous mixing and

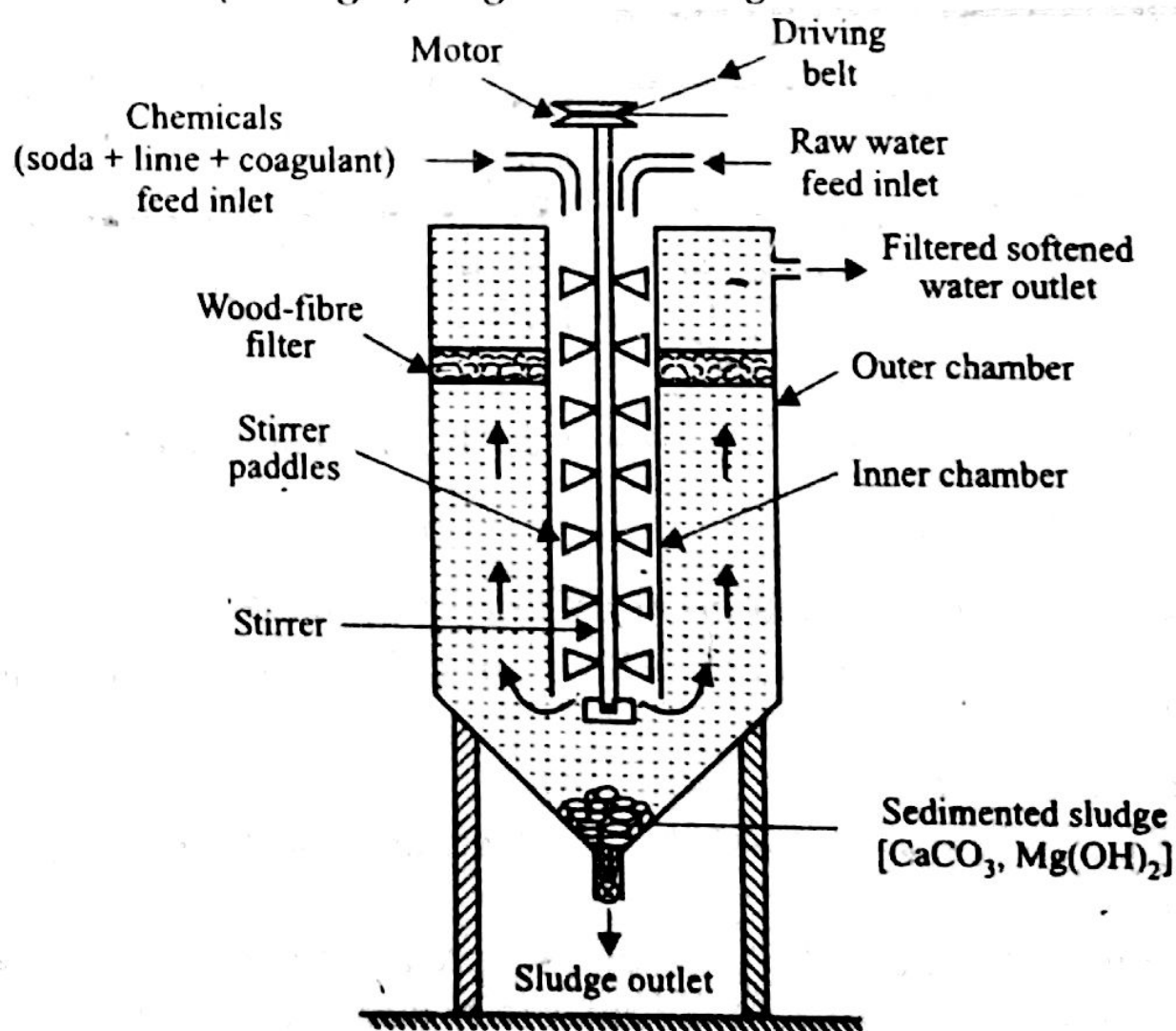


Fig. 9. Continuous cold lime-soda softener.

thus as the raw water and chemicals flow down, softening of water takes place. The softened water is allowed to come into the outer co-axial chamber. The softened water rising up passes through a wood-fiber filter whereby traces of sludges are removed. The sludge settles down in the bottom of outer chamber by the time the softened water reaches up from where it is periodically removed through the sludge outlet. Filtered soft water comes out continuously through the filtered softened water outlet at the top.

(ii) **The sludge-blanket Type.** This process is similar to the above process with a difference that the treated water is filtered upwardly through a suspended sludge blanket composed of previously formed precipitates. This ensures complete utilization of the added lime. But some lime is wasted in the conventional type as it is carried down in the sludge formed by the precipitates before it has time for dissolution and reaction. Silica is removed better in sludge-blanket type. Moreover, the retention period required is just one hour as against four hours with the conventional type softeners.

(iii) **Catalyst or spiractor type cold lime-soda water softener.** This softener consists of a conical tank which may be open (for gravity operation) or closed (for operation under pressure). About two-third of the conical tank is filled with finely divided granular catalyst (0.3 to 0.6 mm diameter) which can be green sand or sand or graded calcite. Inlets for raw water and chemicals are provided near the bottom of the tank. The outlet for soft water is at the top, see Fig. 10.

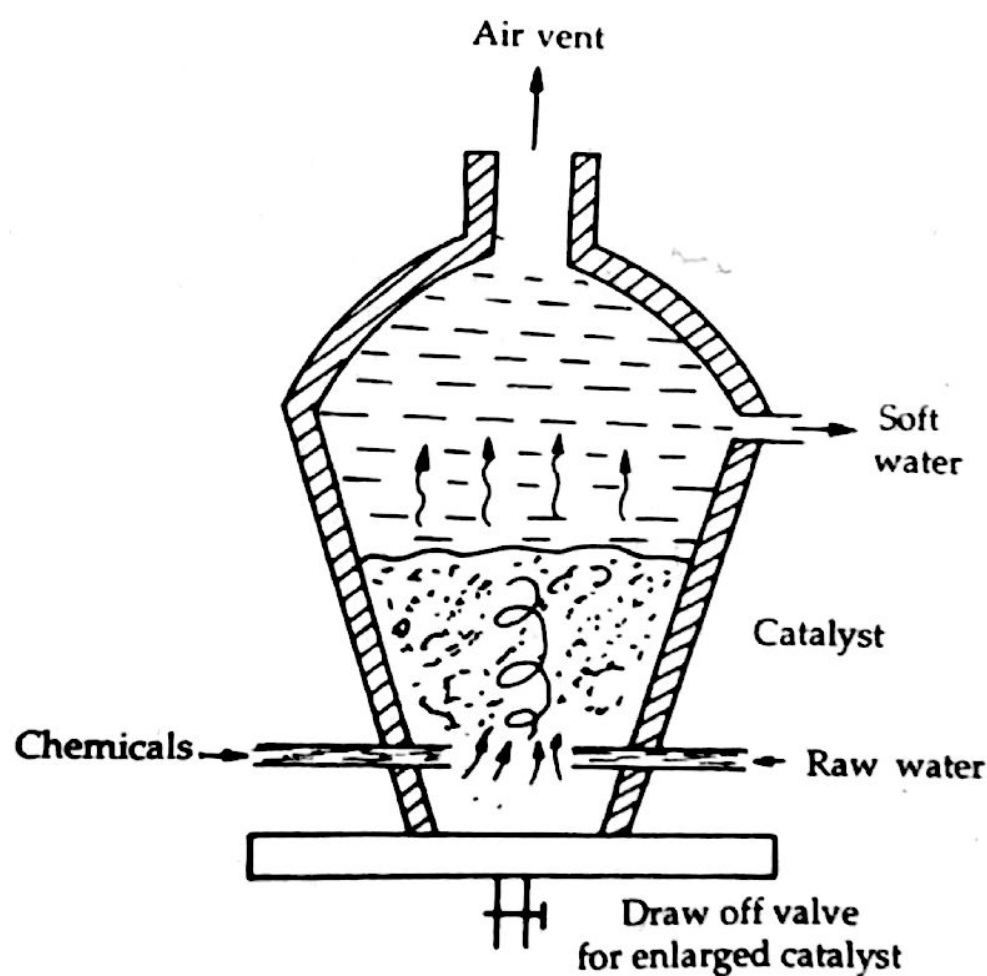


Fig. 10. Catalyst or Spiractor type softener.

**Method.** The raw water and chemicals enter the tank tangentially near the bottom and spiral upwards through the suspended catalyst bed. The sludge formed deposits on the granular catalyst in an adherent form and hence the granules grow in size. The softened water rises to the top from where it is drawn off. It is to be noted that sludge is formed in the granular shape which drain and dries rapidly and can be handled easily.



## (II) Hot Lime-Soda Process

In these processes water is treated with chemicals at a temperature of  $94^{\circ} - 100^{\circ} \text{C}$ . The softeners used may be of the intermittent type or continuous type. These are briefly discussed below :

(a) *The intermittent type (Batch process) Hot lime-soda softener.* It is similar to the intermittent type cold lime-soda softener except that the heating coils are installed in it for heating water.

(b) *The continuous type Hot lime-soda softeners.* This softener essentially consists of three parts :

(i) *Reaction tank.* This tank has three separate inlets, one each for raw water, chemicals and super-heated steam. After all these three are taken in, they are thoroughly mixed. The beginning and completion of reaction occurs in reaction tank.

(ii) *Conical sedimentation tank.* From the reaction tank the contents go to this tank so that sludge settles down.

(iii) *Sand filter.* It has layers of fine and coarse sand which acts as filter and ensures complete removal of sludge from the softened water.

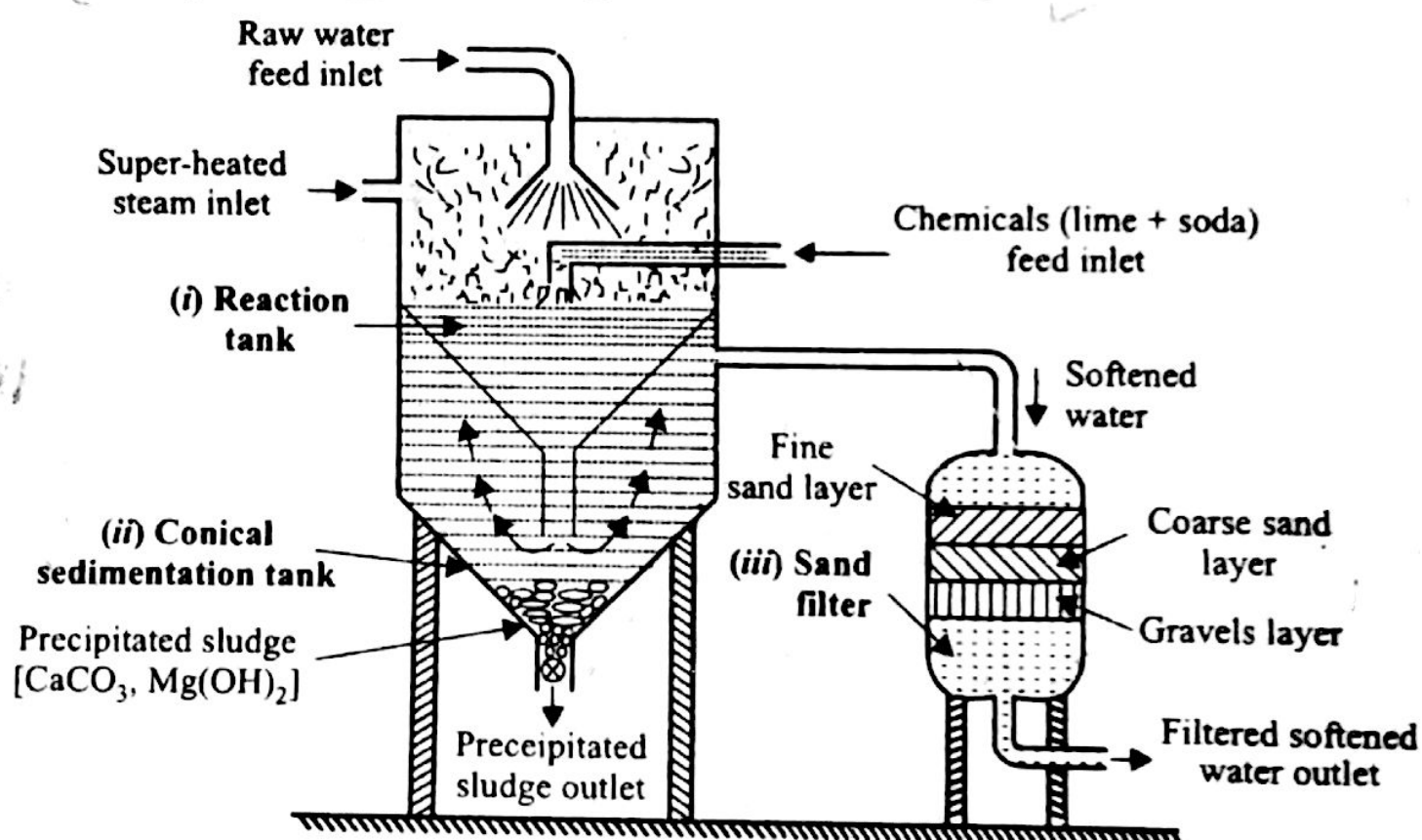


Fig. 11. Continuous hot lime-soda softner.

A soft water with 15-30 ppm of residual hardness is obtained by this process.

*Advantages of Hot Lime-Soda processes.*

(i) These processes are more rapid in operation. The time taken for completion are 15 minutes and several hours for hot and cold lime soda process respectively.

(ii) Elevated temperature accelerates the actual chemical reactions and reduce the viscosity of the water. This increases the rate of aggregation of the particles. Hence, both the settling rates and filtration rates are increased. Thus the softening capacity of the hot process is several times higher than the cold process.

(iii) The sludge and the precipitate formed settle down rapidly and hence no coagulant is needed.

(iv) Quantity of chemicals required for softening is low.

(v) At the higher temperatures, the dissolved gases such as  $\text{CO}_2$  are driven out of the solution to some extent.

(vi) The residual hardness in the softened water is less when it is treated by hot process in comparison to cold lime-soda process.

#### **Advantages of Lime-soda Process**

- (i) Lime-soda process is very economical,
- (ii) Treated water is alkaline and hence has less corrosion tendencies,
- (iii) It removes not only hardness causing salts but also minerals,
- (iv) Due to alkaline nature of treated water, amount of pathogenic bacteria in water is considerably reduced.
- (v) Iron and manganese are also removed from the water to some extent.

#### **Disadvantages of Lime-Soda Process**

- (i) It requires careful operation and skilled supervision for economical and efficient softening.
- (ii) Sludge disposal is a problem.
- (iii) Water softened by this process contains appreciable concentrations of soluble salts, such as sodium sulfate, and cannot be used in high pressure boilers.

The main differences between cold and hot lime soda processes are summarized in Table 7.

**Table 7 : Differences between the Hot and Cold lime-soda process**

S.No.	Cold Lime Soda Process	Hot Lime Soda Process
1.	It is done at room temperature. (25 – 30 °C)	It is done at elevated temperatures (94 – 100° C).
2.	It is a slow process.	It is a rapid process.
3.	The use of coagulants is must.	Coagulants not needed.
4.	Filtration is not easy.	Filtration is easy as the viscosity of water becomes low at elevated temperatures.
5.	Softened water has residual hardness around 60 ppm.	Softened water has residual hardness of 15-30 ppm.
6.	Dissolved gases are not removed.	Dissolved gases such as $\text{CO}_2$ are removed to some extent.
7.	Low softening capacity.	High softening capacity.

#### **Requirements of Lime and Soda**

1. For water softening by lime-soda process, if the given hard water contains calcium salts as the hardness causing impurities then calculated amounts of lime and/or soda are added to this hard water so as to convert soluble calcium salts into insoluble precipitates of calcium carbonate which subsequently are filtered off.

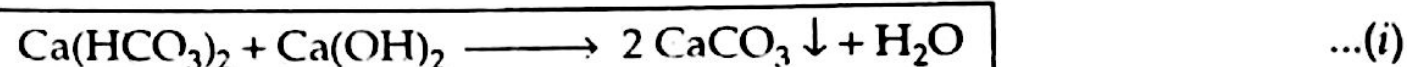


Few specific situations are discussed below :

(i) Suppose the given water has **temporary calcium hardness** due to the presence of calcium bicarbonate.

We know that, if  $\text{OH}^-$  ions are added to an alkaline water containing  $\text{HCO}_3^-$  ions, immediately they will chemically react together to form  $\text{CO}_3^{2-}$  ions.

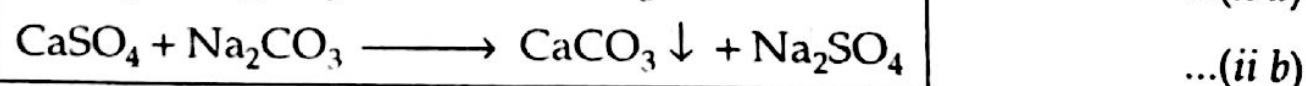
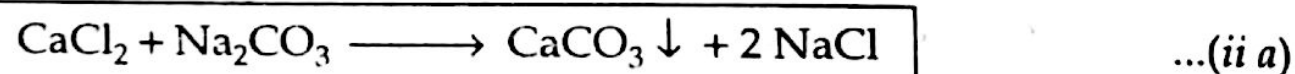
Thus, for the treatment of calcium bicarbonate, we can add calcium hydroxide (i.e., Lime). Because of their immediate chemical reaction, insoluble precipitates of calcium carbonate will form which subsequently are filtered off. The water softening will occur as per the following reaction :



So, we can conclude that *we require only one mole of lime for the softening of hard water containing one mole of calcium bicarbonate.*

(ii) Suppose the given water has **permanent calcium hardness** due to the presence of say calcium chloride, calcium sulphate etc.

For the softening of this hard water, we need to add sodium carbonate (i.e., soda) which will lead to the formation of insoluble precipitate of calcium carbonate as per the following chemical reactions :



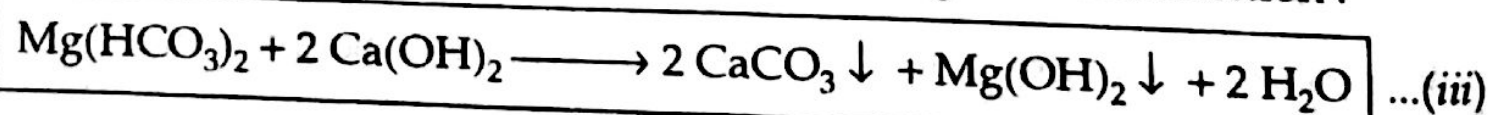
So, we can conclude that *we require one mole of soda for the softening of hard water containing either one mole of calcium chloride or one mole of calcium sulphate.*

2. For water softening by lime-soda process, if the given hard water contains **magnesium salts** as the hardness causing impurities then calculated amount of lime is added to this hard water so as to convert soluble magnesium salts into **insoluble precipitates of magnesium hydroxide** which subsequently are filtered off.

Few specific situations are discussed below :

(i) Suppose the given water has **temporary magnesium hardness** due to the presence of magnesium bicarbonate. For water treatment, we can add lime. This is because magnesium bicarbonate and calcium hydroxide will immediately react together to form insoluble precipitates of magnesium hydroxide and calcium carbonate which can be subsequently filtered off.

The water softening will occur as per the following chemical reaction :



So, we can conclude that *we require two moles of lime for the softening of hard water containing one mole of magnesium bicarbonate.*

Requirement of lime for 1 mol  $\text{Mg (HCO}_3)_2 \equiv 2 \text{ mol Ca(OH)}_2$

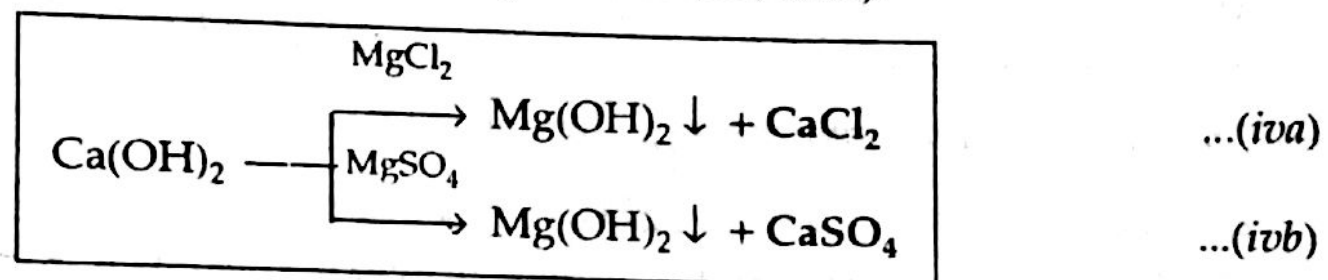
Requirement of lime for 146 gm  $\text{Mg (HCO}_3)_2 \equiv 2 \times 74 \text{ gm}$

Requirement of lime for 1 gm  $\text{Mg}(\text{HCO}_3)_2 \equiv \frac{2 \times 74}{146} \text{ gm}$

Requirement of lime for y ppm  $\text{Mg}(\text{HCO}_3)_2 \equiv 2 \times \frac{74}{146} \times y \text{ ppm}$   
 $\equiv \frac{74}{100} \left[ 2y \times \frac{100}{146} \right] \equiv \frac{74}{100} \left[ 2 \text{ Mg}(\text{HCO}_3)_2 \text{ as CaCO}_3 \text{ eq.} \right] \frac{\text{mg}}{\text{L}}$

(ii) Suppose the given water has permanent magnesium hardness due to the presence of magnesium chloride and/or magnesium sulphate etc.

As magnesium salts must be converted into insoluble magnesium hydroxide precipitates so we need to add calcium hydroxide (i.e., lime).



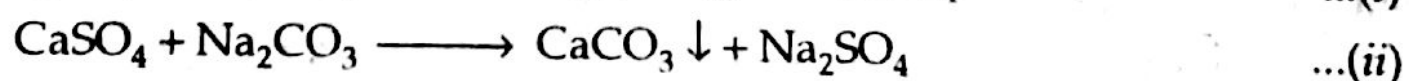
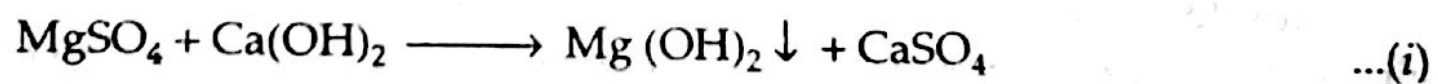
As per the above reactions, although permanent magnesium hardness has been removed by the addition of lime but simultaneously we have generated permanent calcium hardness (i.e., calcium chloride and calcium sulphate).

Thus, for the complete softening, we also need to add soda so that permanent calcium hardness can also be removed as per the equations (ii a) and (ii b).

So, we can conclude that we require one mole of lime and one mole of soda for the complete treatment of one mole of permanent magnesium hardness.

**Illustration 1.** Calculate the amount of lime required for softening of 5000 Litres of hard water containing 72 ppm of  $\text{MgSO}_4$ .

**Solution.** Given hard water contains  $\text{MgSO}_4$  so for its softening we require both lime and soda, according to the equations.



Since only amount of lime has to be calculated in this problem, so Equation (i) is important.

Requirement of lime for 1 mole of  $\text{MgSO}_4 \equiv 1 \text{ mole Ca(OH)}_2$

or requirement of lime for 120 gm of  $\text{MgSO}_4 \equiv 74 \text{ gm Ca(OH)}_2$

$\therefore$  Requirement of lime for 72 ppm of  $\text{MgSO}_4 \equiv \frac{74}{120} \times 72 \text{ ppm or mg/L} \quad \dots(iii)$

Hence, for softening of 1L of water, lime required is  $= \frac{74 \times 72}{120} \text{ mg}$

Thus, for softening of 5000L of water, lime required is

$$= \frac{74 \times 72}{120} \times 5000 = 222000 \text{ mg} = 222 \text{ gm.}$$



**Alternative solution.**

From equation (iii), Lime requirement =  $\frac{74}{120} \times 72$

$$= \frac{74}{100} \times \left( 72 \times \frac{100}{120} \right) = \frac{74}{100} (\text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}) \text{ mg/L.}$$

Thus, Lime requirement =  $\frac{74}{100} [\text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}] \times \text{vol. of water (in mg)}$

**Step I. Calculation of CaCO<sub>3</sub> equivalent**

Constituent	Amount	Multiplication factor	CaCO <sub>3</sub> equivalent
MgSO <sub>4</sub>	72 ppm	100/120	$72 \times \frac{100}{120} = 60 \text{ ppm or } 60 \text{ mg/L}$

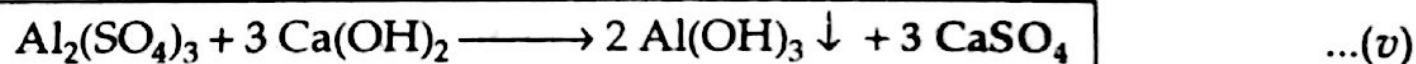
$$\begin{aligned} \text{Step II. Lime requirement} &= \frac{74}{100} [60 \text{ mg/L}] \times 5000 \text{ L} \\ &= 222,000 \text{ mg} = 222 \text{ gm} \end{aligned}$$

3. Aluminium salts may be present in water as contributor of permanent hardness or they may be added as coagulants in cold lime-soda process.

For water softening, these aluminium salts need to be converted into **insoluble aluminium hydroxide precipitates**.

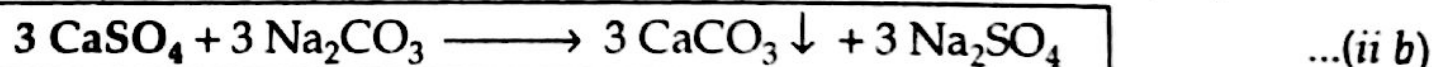
Few specific situations are discussed below :

(i) Suppose the given water has **aluminium sulphate**. For softening, aluminium sulphate has to be converted into insoluble Al(OH)<sub>3</sub> precipitate. Thus, we need to add lime.



As per the above softening reaction, although permanent aluminium hardness has been removed by the addition of lime but simultaneously we have generated permanent calcium hardness (i.e., calcium sulphate).

Thus, for the complete softening, we also need to add soda so that permanent calcium sulphate hardness can also be removed as per the equation (ii b).



So, we can conclude that *we require three moles of lime and three moles of soda for the complete treatment of hard water, containing one mole of aluminium sulphate.*

Requirement of lime for 1 mole Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  $\equiv$  3 mole Ca(OH)<sub>2</sub>  
 or requirement of lime for 342 gm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  $\equiv$  3  $\times$  74 gm Ca(OH)<sub>2</sub>  
 requirement of lime for 1 gm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  $\equiv$   $\frac{3 \times 74}{342}$  gm Ca(OH)<sub>2</sub>

Thus for x ppm Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, requirement of lime =  $\frac{74}{114} \times x \text{ ppm or mg/L}$

$$\frac{74}{100} \left( x \times \frac{100}{114} \right) = \frac{74}{100} (\text{Al}_2(\text{SO}_4)_3 \text{ as CaCO}_3 \text{ eq.}) \text{ mg/L}$$

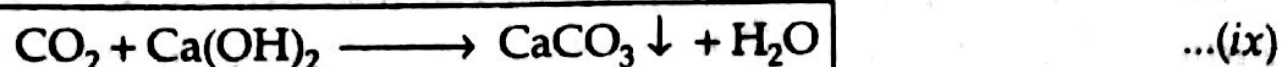
(ii) Suppose the coagulant added in cold-lime-soda process is **sodium aluminate**. In water, it will undergo hydrolysis to form insoluble precipitate of aluminium hydroxide and simultaneously sodium hydroxide is also generated.





6. For the treatment of carbonated water (i.e., water containing dissolved carbon dioxide), we need to add only lime.

The softening reaction is as follows :



Thus, we can conclude that for the treatment of one mole of  $\text{CO}_2$ , we require one mole of lime.

7. For the treatment of alkaline water, containing sodium bicarbonate, lime is required to be added. This is because  $\text{HCO}_3^-$  ions (from sodium bicarbonate) and  $\text{OH}^-$  ions (from calcium hydroxide) will immediately react together to form  $\text{CO}_3^{2-}$  ions. Thus, insoluble precipitates of calcium carbonate will be formed as per the following reaction :



As can be seen from above equation (x), soda is also generated as one of the products.

Thus, we can conclude that for the treatment of 2 moles of  $\text{NaHCO}_3$  alkalinity, one mole of lime is required and one mole of soda is also generated.

A given hard water sample may contain any combination of different salts or ions. Accordingly, it requires different quantities of lime and soda for effective softening. The various constituents, their chemical reactions with lime and/or soda is summarized in Table 8.

**Lime-requirement for softening (in mg/L)**

$$= \frac{74}{100} \left[ \left( \begin{array}{c} \text{Ca(HCO}_3)_2 \\ \text{or} \\ \text{Temp. Ca}^{2+} \end{array} \right) + \left( \begin{array}{c} 2\text{Mg(HCO}_3)_2 \\ \text{or} \\ 2 \times \text{Temp. Mg}^{2+} \end{array} \right) \right. \\ \left. + \text{Perm.} \left\{ \left( \begin{array}{c} \text{Mg}^{2+} \\ \text{or} \\ \text{MgCl}_2 \text{ or } \text{MgSO}_4 \end{array} \right) + \left( \begin{array}{c} \text{Fe}^{2+} \text{ or } \text{FeSO}_4 \\ \text{or} \\ \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \end{array} \right) + \left( \begin{array}{c} \text{Al}^{3+} \\ \text{or} \\ \text{Al}_2(\text{SO}_4)_3 \end{array} \right) \right\} \right. \\ \left. + \text{CO}_2 + \left( \begin{array}{c} \text{H}^+ \text{ or } \text{HCl} \\ \text{or} \\ \text{H}_2\text{SO}_4 \end{array} \right) + \left( \begin{array}{c} \text{HCO}_3^- \\ \text{or} \\ \text{NaHCO}_3 \end{array} \right) - \text{NaAlO}_2 \right] \text{ all in terms of CaCO}_3 \text{ equivalents}$$

**and Soda requirement for softening (in mg/L)**

$$= \frac{106}{100} \left[ \text{perm.} \left\{ \left( \begin{array}{c} \text{Ca}^{2+} \text{ or } \text{CaCl}_2 \\ \text{or} \\ \text{CaSO}_4 \end{array} \right) + \left( \begin{array}{c} \text{Mg}^{2+} \text{ or } \text{MgCl}_2 \\ \text{or} \\ \text{MgSO}_4 \end{array} \right) \right. \right. \\ \left. \left. + (\text{Al}^{3+} \text{ or } \text{Al}_2(\text{SO}_4)_3 + \left( \begin{array}{c} \text{Fe}^{2+} \\ \text{or} \\ \text{FeSO}_4 \end{array} \right) \right\} + \left( \begin{array}{c} \text{H}^+ \\ \text{or} \\ \text{HCl or H}_2\text{SO}_4 \end{array} \right) - \left( \begin{array}{c} \text{HCO}_3^- \\ \text{or} \\ \text{or NaHCO}_3 \end{array} \right) \right]$$

all in terms of  $\text{CaCO}_3$  equivalents.

Table 8

S.No.	Constituent	Reactions	Need
1	Ca(HCO <sub>3</sub> ) <sub>2</sub> (Temp. Ca)	Ca (HCO <sub>3</sub> ) <sub>2</sub> + Ca(OH) <sub>2</sub> → 2 CaCO <sub>3</sub> ↓ + H <sub>2</sub> O	L
2	Mg(HCO <sub>3</sub> ) <sub>2</sub> (Temp. Mg)	Mg (HCO <sub>3</sub> ) <sub>2</sub> + 2 Ca(OH) <sub>2</sub> → 2 CaCO <sub>3</sub> ↓ + Mg(OH) <sub>2</sub> + 2 H <sub>2</sub> O	2L
3	Mg <sup>2+</sup> (Perm. Mg From MgCl <sub>2</sub> or MgSO <sub>4</sub> )	Mg <sup>2+</sup> + Ca(OH) <sub>2</sub> → Mg(OH) <sub>2</sub> ↓ + Ca <sup>2+</sup> Ca <sup>2+</sup> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> ↓ + 2 Na <sup>+</sup>	L S
	or more specifically	MgCl <sub>2</sub> + Ca(OH) <sub>2</sub> → Mg(OH) <sub>2</sub> ↓ + CaCl <sub>2</sub> CaCl <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> ↓ + 2 NaCl	(L + S)
	and	MgSO <sub>4</sub> + Ca(OH) <sub>2</sub> → Mg(OH) <sub>2</sub> ↓ + CaSO <sub>4</sub> CaSO <sub>4</sub> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> ↓ + Na <sub>2</sub> SO <sub>4</sub>	(L + S)
4	HCO <sub>3</sub> <sup>-</sup> (e.g., NaHCO <sub>3</sub> )	2NaHCO <sub>3</sub> + Ca(OH) <sub>2</sub> → CaCO <sub>3</sub> ↓ + H <sub>2</sub> O + Na <sub>2</sub> CO <sub>3</sub>	(L - S)
5	Ca <sup>2+</sup> (Perm. Ca From CaCl <sub>2</sub> or CaSO <sub>4</sub> )	Ca <sup>2+</sup> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> ↓ + 2 Na <sup>+</sup>	S
	or more specially :	CaCl <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> ↓ + 2 NaCl CaSO <sub>4</sub> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> ↓ + Na <sub>2</sub> SO <sub>4</sub>	S



S.No.	Constituent	Reactions	Need
6.	CO <sub>2</sub>	$\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	L
7.	H <sup>+</sup> (free acids like HCl, H <sub>2</sub> SO <sub>4</sub> , etc.)  or more specifically :	$2\text{H}^+ + \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$  $2\text{HCl} + \text{Ca(OH)}_2 \rightarrow \text{CaCl}_2 + 2\text{H}_2\text{O}$ $\text{H}_2\text{SO}_4 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{NaCl}$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	(L + S)  L L S S
Note : Aluminium and Iron salt may be present in water as contributor of Permanent hardness or they may be added as coagulants.			
8.	FeSO <sub>4</sub>	$\text{FeSO}_4 + \text{Ca(OH)}_2 \rightarrow \text{Fe(OH)}_2 + \text{CaSO}_4$ $2\text{Fe(OH)}_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe(OH)}_3 \downarrow$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$	(L + S)
9.	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	$\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3 \downarrow + 3\text{CaSO}_4$ $3\text{CaSO}_4 + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 \downarrow + 3\text{Na}_2\text{SO}_4$	(L + S)
10.	NaAlO <sub>2</sub>	$\text{NaAlO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 \downarrow + \text{NaOH}$	-1 L

**Notes.**

1. Substances like NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> etc. do not impart any hardness and therefore, these do not consume any lime or soda. These should not be taken into consideration for calculating the lime and soda requirements.
2. All the substances causing hardness should be converted into their respective CaCO<sub>3</sub> equivalent. For this multiplication factors are required. Multiplication factors for some of the impurities in water which we commonly come across are given in table 8.

**Solved Numerical Examples for The Determination of Requirement of Lime & Soda**

**Example 1.** Calculate the amount of lime required for softening 50,000 litres of hard water containing : Mg(HCO<sub>3</sub>)<sub>2</sub> = 144 ppm ; Ca(HCO<sub>3</sub>)<sub>2</sub> = 25 ppm ; MgCl<sub>2</sub> = 95 ppm, CaCl<sub>2</sub> = 111 ppm ; Fe<sub>2</sub>O<sub>3</sub> = 25 ppm ; Na<sub>2</sub>SO<sub>4</sub> = 15 ppm

**Solution.** Suppose, L stands for Lime Ca(OH)<sub>2</sub>  
and S stands for soda Na<sub>2</sub>CO<sub>3</sub>.

Constituent	Reactions	Need
Mg(HCO <sub>3</sub> ) <sub>2</sub>	Mg (HCO <sub>3</sub> ) <sub>2</sub> + 2 Ca (OH) <sub>2</sub> → 2 CaCO <sub>3</sub> ↓ + Mg(OH) <sub>2</sub> ↓ + 2 H <sub>2</sub> O	2L
Ca(HCO <sub>3</sub> ) <sub>2</sub>	Ca(HCO <sub>3</sub> ) <sub>2</sub> + Ca(OH) <sub>2</sub> → 2 Ca(CO <sub>3</sub> ) ↓ + 2 H <sub>2</sub> O	L
MgCl <sub>2</sub>	MgCl <sub>2</sub> + Ca(OH) <sub>2</sub> → Mg(OH) <sub>2</sub> ↓ + CaCl <sub>2</sub>	L
CaCl <sub>2</sub>	CaCl <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub> → CaCO <sub>3</sub> ↓ + 2 NaCl	S

Moreover, Fe<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> does not causes hardening so they do not need L or S.

$$\text{Thus, Lime requirement} = \frac{74}{100} [2 \times \text{Mg (HCO}_3)_2 + \text{Ca(HCO}_3)_2 + \text{MgCl}_2 \text{ in terms of CaCO}_3 \text{ eq.}] \times \text{volume of water}$$

**Step I.** Conversion into CaCO<sub>3</sub> equivalents

Constituent	Amount	Multiplication factor	CaCO <sub>3</sub> equivalent
Mg(HCO <sub>3</sub> ) <sub>2</sub>	144 ppm	100/146	$144 \times \frac{100}{146} = 98.6 \text{ ppm}$
Ca(HCO <sub>3</sub> ) <sub>2</sub>	25 ppm	100/162	$25 \times 100/162 = 15.4 \text{ ppm}$
MgCl <sub>2</sub>	95 ppm	100/95	$95 \times 100/95 = 100 \text{ ppm}$

$$\begin{aligned} \text{Step II. Lime requirement} &= \frac{74}{100} [2 \times 98.6 + 15.4 + 100] \text{ mg/L} \times 50,000 \text{ L} \\ &= 1156200 \text{ mg} = 11.57 \text{ kg} \end{aligned}$$

**Example 2.** Analysis of water gave the following results. H<sub>2</sub>SO<sub>4</sub> = 196 mg/l, MgSO<sub>4</sub> = 24 mg/l, CaSO<sub>4</sub> = 272 mg/l and NaCl = 25 mg/l. Water is to be supplied to the town of the population of one lakh only. The daily consumption of water is 50 litre per head. Calculate the cost of lime and soda required for the softening the hard water for town for the month April 2002. If the cost of lime is Rs. 5.00 per kg and cost of soda is Rs. 8.00 per kg.



**Solution.** Lime requirement per day

$$\begin{aligned}
 &= \frac{74}{100} [\text{H}_2\text{SO}_4 + \text{MgSO}_4 \text{ as CaCO}_3 \text{ eq}] \times \text{vol. of water} \\
 &= \frac{74}{100} \left[ 196 \times \frac{100}{98} + 24 \times \frac{100}{120} \right] \text{mg/L} \times \underbrace{50 \text{ L/head}}_{\text{Per person water requirement}} \times \underbrace{1,00,000 \text{ persons}}_{\text{Total persons}} \times \underbrace{\frac{1 \text{ kg}}{10^6 \text{ mg}}}_{\text{Conversion of mg into kg}}
 \end{aligned}$$

$$= 814 \text{ kg.}$$

For the April 2002 month (30 days), total lime requirement

$$= 814 \times 30 = 24420 \text{ kg.}$$

Given cost of lime = Rs. 5.00/kg.

$$\therefore \text{Total cost of lime} = 24420 \text{ kg} \times \frac{5 \text{ Rs.}}{\text{kg}} = 1,22,100 \text{ Rs.}$$

Similarly, cost of soda

$$\begin{aligned}
 &= \frac{106}{100} [\text{H}_2\text{SO}_4 + \text{MgSO}_4 + \text{CaSO}_4 \text{ as CaCO}_3 \text{ eq}] \text{mg/L} \times 50 \times 10^5 \text{ L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times 30 \times \frac{\text{Rs. } 8}{\text{kg}} \\
 &= \frac{106}{100} \left[ 196 \times \frac{100}{98} + 24 \times \frac{100}{120} + 272 \times \frac{100}{136} \right] \times 50 \times 10^5 \times \frac{1}{10^6} \times 30 \times 8 = 5,34,240 \text{ Rs.}
 \end{aligned}$$

**Example 3.** A sample of water was analysed and found to contain temporary magnesium hardness 25 mg/lt. permanent magnesium chloride hardness 15 mg/lt. and permanent calcium sulphate hardness 20 mg/lt.,  $\text{SiO}_2 = 300 \text{ mg/lt.}$  Calculate the lime and soda required for softening 30,000 litres of hard water.

**Solution.** Lime requirement

$$\begin{aligned}
 &= \frac{74}{100} [2 \times \text{temp. Mg} + \text{MgCl}_2 \text{ as CaCO}_3 \text{ eq.}] \times \text{vol. of water} \\
 &= \frac{74}{100} \left[ 2 \times 25 \times \frac{100}{24} + 15 \times \frac{100}{95} \right] \text{mg/L} \times 30,000 \text{ L} \times \frac{1 \text{ gm}}{10^3 \text{ mg}} = 4975.53 \text{ gm.}
 \end{aligned}$$

$$\text{Soda Requirement} = \frac{106}{100} [\text{MgCl}_2 + \text{CaSO}_4 \text{ as CaCO}_3 \text{ eq.}] \times \text{vol. of water}$$

$$= \frac{106}{100} \left[ 15 \times \frac{100}{95} + 20 \times \frac{100}{136} \right] \text{mg/L} \times 30,000 \text{ L} \times \frac{1 \text{ gm}}{10^3 \text{ mg}} = 969.75 \text{ gm.}$$

**Example 4.** Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20,000 litres of water, whose analysis is as follows :

$\text{Ca}(\text{HCO}_3)_2 = 40.5 \text{ ppm}$  ;  $\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}$  ;  $\text{MgSO}_4 = 30.0 \text{ ppm}$  ;  
 $\text{CaSO}_4 = 34.0 \text{ ppm}$  ;  $\text{CaCl}_2 = 27.75 \text{ ppm}$  and  $\text{NaCl} = 10.00 \text{ ppm}$ .

Also calculate the temporary and permanent hardness of water sample.

**Solution.** Temporary hardness

$$= \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 = 40.5 \times \frac{100}{162} + 36.5 \times \frac{100}{146} = 50 \text{ ppm.}$$

## Permanent hardness

1.63

$$= \text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2 = 30 \times \frac{100}{120} + 34 \times \frac{100}{136} + 27.75 \times \frac{100}{111} = 75 \text{ ppm}$$

As the supplied lime (84% pure) and soda (92% pure) are impure, therefore, the exact lime and soda requirement calculation needs multiplication by purity factors of  $\frac{100}{84}$  for lime and  $\frac{100}{92}$  for soda.

$$\begin{aligned} \text{Lime } & \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2\text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4] \\ &= \frac{74}{100} \left[ 40.5 \times \frac{100}{162} + 2 \times 36.5 \times \frac{100}{146} + 30 \times \frac{100}{120} \right] \times \frac{20,000}{10^6} \times \frac{100}{84} \text{ kg} = 1.762 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Soda } &= \frac{106}{100} [\text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2] \times \frac{20,000}{10^6} \times \frac{100}{92} \text{ kg} \\ &= \frac{106}{100} \left[ 30 \times \frac{100}{120} + 34 \times \frac{100}{136} + 27.25 \times \frac{100}{111} \right] \times \frac{20,000}{10^6} \times \frac{100}{92} = 1.728 \text{ kg.} \end{aligned}$$

**Example 5.** Explain with chemical equations and calculate the amount of lime and soda needed for softening 1,00,000 litres of water containing the following per litre :

- (i)  $\text{HCl} = 7.3 \text{ mg/l}$  ; (ii)  $\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ mg/l}$  ;  
 (iii)  $\text{MgCl}_2 = 9.5 \text{ mg/l}$  ; (iv)  $\text{NaCl} = 29.25 \text{ mg/l}$ .

Purity of lime is 90% and that of soda is 98%. 10% of chemicals are to be used in excess in order to complete the reaction quickly.

**Solution.** Lime requirement

$$\begin{aligned} &= \frac{74}{100} [\text{HCl} + \text{Al}_2(\text{SO}_4)_3 + \text{MgCl}_2 \text{ as } \text{CaCO}_3 \text{ eq.}] \times \text{vol. of water} \\ &= \frac{74}{100} \left[ 7.3 \times \frac{100}{73} + 34.2 \times \frac{100}{114} + 9.5 \times \frac{100}{95} \right] \text{ mg/L} \times 1,00,000 \text{ L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = 3.7 \text{ kg.} \end{aligned}$$

As lime is 90% pure and 10% excess of it was used, so the actual amount of lime needed for softening =  $3.7 \times \frac{100}{90} \times \frac{110}{100} = 4.52 \text{ kg}$

Soda requirement

$$\begin{aligned} &= \frac{106}{100} [\text{HCl} + \text{Al}_2(\text{SO}_4)_3 + \text{MgCl}_2 \text{ as } \text{CaCO}_3 \text{ eq.}] \times \text{vol. of water} \\ &= \frac{106}{100} \left[ 7.3 \times \frac{100}{73} + 34.2 \times \frac{100}{114} + 9.5 \times \frac{100}{95} \right] \text{ mg/L} \times 100,000 \text{ L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = 5.3 \text{ kg.} \end{aligned}$$

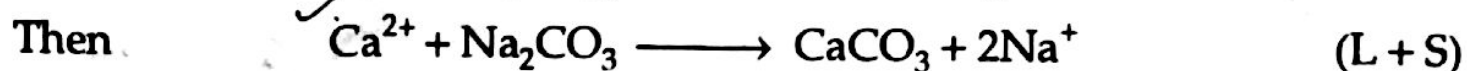
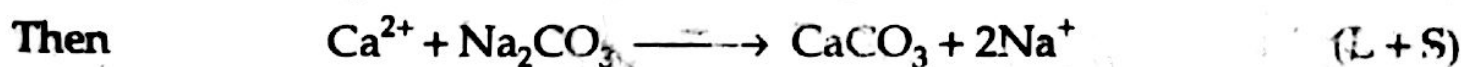
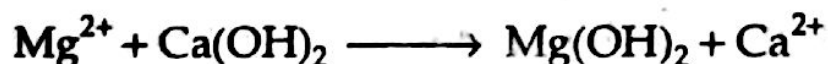
And actual amount of soda needed for softening =  $5.3 \times \frac{100}{98} \times \frac{110}{100} = 5.95 \text{ kg.}$

**Example 6.** Explain with equations and calculate the quantity of quick lime and soda ash required to soften 10,000 litres of water containing :

- (i) 219 ppm of magnesium bicarbonate and 234 ppm of sodium chloride ;  
 (ii) 36 ppm of  $\text{Mg}^{2+}$  and 18.3 ppm of  $\text{HCO}_3^-$   
 (iii) 1.5 ppm of the free acids, 144 ppm of sulphate ions and 71 ppm of chloride ions.



**Solution.** Lime requirement for  $\text{Mg}(\text{HCO}_3)_2$  is two equivalents, the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions are treated as permanent hardness causing ions. Moreover,  $\text{NaCl}$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions which do not contribute toward hardness are ignored while calculating lime and soda requirement.



$$\text{Lime} = \frac{74}{100} [2 \text{Mg}(\text{HCO}_3)_2 + \text{Mg}^{2+} + \text{HCO}_3^- + \text{H}^+] \times \frac{10,000}{10^6} \text{ kg}$$

$$= \frac{74}{100} \left[ 2 \times 219 \times \frac{100}{146} + 36 \times \frac{100}{24} + 18.3 \times \frac{100}{122} + 1.5 \times \frac{100}{2} \right] \times \frac{1}{100} = 3.996 \text{ kg}$$

$$\text{Soda} = \frac{106}{100} [\text{Mg}^{2+} - \text{HCO}_3^- + \text{H}^+] \times \frac{10,000}{10^6} \text{ kg}$$

$$= \frac{106}{100} \left[ 36 \times \frac{100}{24} - 18.3 \times \frac{100}{122} + 1.5 \times \frac{100}{2} \right] \times \frac{1}{100} = 2.226 \text{ kg.}$$

**Example 7.** Calculate the amount of lime and soda required for softening one million litres of water containing :

$\text{H}^+$  (Free acidity) = 1.5 ppm ;  $\text{HCO}_3^- = 396.5 \text{ ppm}$  ;  $\text{Mg}^{+2} = 42.0 \text{ ppm}$  ;  $\text{Ca}^{+2} = 90.00 \text{ ppm}$  ;  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O} = 14 \text{ ppm}$ .

The purity of lime is 91% and that of soda is 97.2%. Given Atomic mass of :  $\text{H} = 1$ ,  $\text{Na} = 23$ ,  $\text{Ca} = 40$ ,  $\text{Mg} = 24$ ,  $\text{O} = 16$ ,  $\text{C} = 12$ ,  $\text{S} = 32$ ,  $\text{Fe} = 56$ .

**Solution.** Lime requirement

$$\begin{aligned} &= \frac{74}{100} [\text{H}^+ + \text{HCO}_3^- + \text{Mg}^{2+} + \text{FeSO}_4 \cdot 7 \text{H}_2\text{O as CaCO}_3 \text{ eq.}] \times \text{vol. of water} \times \frac{100}{91} \\ &= \frac{74}{100} \left[ 1.5 \times \frac{100}{2} + 396.5 \times \frac{100}{122} + 42 \times \frac{100}{24} + 14 \times \frac{100}{278} \right] \text{mg/L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times 10^6 \text{ L} \times \frac{100}{91} \\ &= 471.67 \text{ kg.} \end{aligned}$$

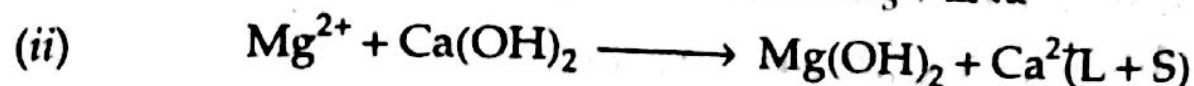
Soda requirement

$$\begin{aligned} &= \frac{106}{100} [\text{H}^+ - \text{HCO}_3^- + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{FeSO}_4 \cdot 7 \text{H}_2\text{O as CaCO}_3 \text{ eq.}] \times V \times \frac{100}{97.2} \\ &= \frac{106}{100} \left[ 1.5 \times \frac{100}{2} - 396.5 \times \frac{100}{122} + 42 \times \frac{100}{24} + 90 \times \frac{100}{40} + 14 \times \frac{100}{278} \right] \text{mg/L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times 10^6 \text{ L} \times \frac{100}{97.2} \\ &= 169.07 \text{ kg.} \end{aligned}$$

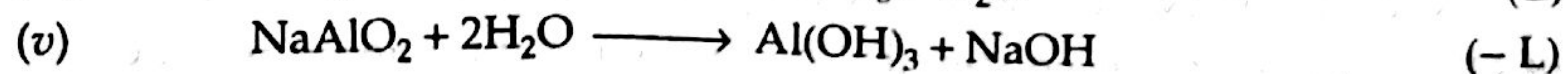
**Example 8.** Calculate the quantities of lime and soda required for softening 300,000 litres of water, using 32.8 ppm of sodium aluminate as a coagulant. Impurities in water are as follows :

$\text{Ca}^{2+} = 240 \text{ ppm}$  ;  $\text{Mg}^{2+} = 96 \text{ ppm}$  ;  $\text{HCO}_3^- = 732 \text{ ppm}$  ; dissolved  $\text{CO}_2 = 44 \text{ ppm}$  ;  $\text{NaCl} = 60 \text{ ppm}$  ;  $\text{Fe}_2\text{O}_3 = 160 \text{ ppm}$ .

[RGPV, Dec. 2003]



$\therefore$  S is required for  $\text{Ca}^{2+}$



$$\begin{aligned} \text{Lime} &= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 - \text{NaAlO}_2] \times \frac{V}{10^6} \text{ kg} \\ &= \frac{74}{100} \left[ 96 \times \frac{100}{24} + 732 \times \frac{100}{122} + 44 \times \frac{100}{44} - 32.8 \times \frac{100}{164} \right] \times \frac{3 \times 10^5}{10^6} \text{ kg} \\ &= 239.76 \text{ kg.} \end{aligned}$$

$$\begin{aligned} \text{Soda} &= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^-] \times \frac{V}{10^6} \times \text{kg} \\ &= \frac{106}{100} \left[ 240 \times \frac{100}{40} + 96 \times \frac{100}{24} - 732 \times \frac{100}{122} \right] \times \frac{3 \times 10^5}{10^6} \text{ kg} \\ &= 127.2 \text{ kg.} \end{aligned}$$

**Example 9.** Calculate the quantities of lime  $[\text{Ca}(\text{OH})_2]$  and soda (anhyd.  $\text{Na}_2\text{CO}_3$ ) required for cold softening of 125,000 L of water with the following analysis, using 10 ppm of sodium aluminate as coagulant :

Analysis of raw water :  $\text{Ca}^{2+} = 95 \text{ ppm}$  ;  $\text{Mg}^{2+} = 36 \text{ ppm}$  ;  $\text{CO}_2 = 66 \text{ ppm}$  ;  $\text{HCO}_3^- = 264 \text{ ppm}$  ;  $\text{H}^+ = 2 \text{ ppm}$ .

Analysis of treated water :  $\text{CO}_3^{2-} = 45 \text{ ppm}$  ;  $\text{OH}^- = 34 \text{ ppm}$ . Write the chemical equations involved.

**Solution.** Conversion into  $\text{CaCO}_3$  equivalents

Constituent	Amount (ppm)	Multiplication factor	$\text{CaCO}_3$ equivalent
<b>Raw water</b>			
$\text{Ca}^{2+}$	95	100/40	237.5
$\text{Mg}^{2+}$	36	100/24	150
$\text{HCO}_3^-$	264	100/122	216.4
$\text{CO}_2$	66	100/44	150
$\text{NaAlO}_2$	10	100/164	6.098
$\text{H}^+$	2	100/2	100
<b>Treated water</b>			
$\text{OH}^-$	34	100/34	100
$\text{CO}_3^{2-}$	45	100/60	75

$\therefore$  Amount of lime required for just softening

$$\begin{aligned} &= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}^+ - \text{NaAlO}_2 \text{ as } \text{CaCO}_3 \text{ eq}] \\ &= \frac{74}{100} [150 + 216.4 + 150 + 100 - 6.098] \\ &= 451.6 \text{ ppm.} \end{aligned}$$

...(i)



Amount of soda required for just softening

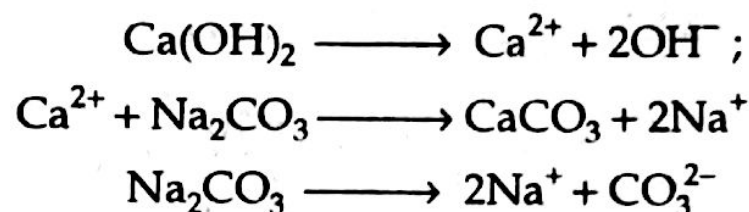
$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{H}^+ - \text{HCO}_3^-]$$

$$= \frac{106}{100} [237.5 + 150 + 100 - 216.4] = 287.4 \text{ ppm.} \quad \dots(ii)$$

As the treated water is shown to contain  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ , the required amount of  $\text{OH}^-$  should have been supplied by its equivalent amount of  $\text{Ca}(\text{OH})_2$ . But, however, the corresponding amount of  $\text{Ca}^{2+}$  so incorporated should have been removed by adding equivalent amount of  $\text{Na}_2\text{CO}_3$ .

The  $\text{CO}_3^{2-}$  required to be present in the treated water must have been supplied by its equivalent amount of  $\text{Na}_2\text{CO}_3$ .

Reactions involved to get excess  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  :



$\therefore$  Lime required for excess  $\text{OH}^-$  in treated water

$$= \frac{74}{100} [\text{OH}^- \text{ as } \text{CaCO}_3 \text{ eq}] = \frac{74}{100} \times 100 = 74 \text{ ppm} \quad \dots(iii)$$

and soda required for excess  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions in treated-water

$$= \frac{106}{100} [\text{OH}^- + \text{CO}_3^{2-}] = \frac{106}{100} [100 + 75] = 185.5 \text{ ppm.} \quad \dots(iv)$$

$\therefore$  Total lime requirement for 125,000 L of water

$$\begin{aligned} &= [(i) + (iii)] \times \frac{125,000}{10^6} \text{ kg} \\ &= (451.6 + 74) \times 0.125 = 65.7 \text{ kg} \end{aligned}$$

Total soda requirement for 125,000 L of water

$$\begin{aligned} &= [(i) + (iv)] \times 0.125 \text{ kg} \\ &= [287.4 + 185.5] \times 0.125 = 59.1 \text{ kg.} \end{aligned}$$

**Example 10.** A sample of hard water was analysed and following results were obtained :  
 $\text{Ca}^{+2} = 70 \text{ ppm}$  ;  $\text{Mg}^{+2} = 30 \text{ ppm}$  ;  $\text{CO}_2 = 22 \text{ ppm}$  ;  $\text{HCO}_3^- = 46.36 \text{ ppm}$  ; Free acidity = 1.5 ppm.

This water is to be softened by lime-soda process at the rate of 5,000 litres of water per minute. For coagulation 13.9 ppm of commercial grade ferrous sulphate ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ) is used as co-agulant. Calculate the quantity of lime and Soda required per hour, the % purity of lime and soda being 80% and 98% respectively.  
 [RGPV, Feb. 2005]

**Solution.** Lime requirement

$$\begin{aligned} &= \frac{74}{100} [\text{Mg}^{2+} + \text{CO}_2 + \text{HCO}_3^- + \text{H}^+ + \text{FeSO}_4 \cdot 7 \text{H}_2\text{O}] \text{ mg/L} \times \text{Rate (L/min)} \times \frac{60 \text{ min}}{\text{hr.}} \times \frac{100}{80} \times \frac{\text{kg}}{10^6 \text{ mg}} \\ &= \frac{74}{100} \left[ 30 \times \frac{100}{24} + 22 \times \frac{100}{44} + 46.36 \times \frac{100}{122} + 1.5 \times \frac{100}{2} + 13.9 \times \frac{100}{278} \right] \times 5000 \times 60 \times \frac{100}{80} \times \frac{1}{10^6} \\ &= 81.3075 \text{ kg/hr.} \end{aligned}$$

## Soda requirement

$$\begin{aligned}
 &= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- + \text{H}^+ + \text{FeSO}_4 \cdot 7\text{H}_2\text{O}] \text{ mg/L} \times \frac{5000 \text{ L}}{\text{min.}} \times \frac{60 \text{ min}}{\text{hr.}} \times \frac{100}{98} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \\
 &= \frac{106}{100} \left[ 70 \times \frac{100}{40} + 30 \times \frac{100}{24} - 46.36 \times \frac{100}{122} + 1.5 \times \frac{100}{2} + 13.9 \times \frac{100}{278} \right] \\
 &= 110.975 \text{ kg/hr.}
 \end{aligned}$$

**Example 11.** Calculate the amount of lime (88.3% pure) and soda (99.2% pure) required to soften 24,000 litres of water per day for a year containing the following:

$\text{CaCO}_3 = 1.85 \text{ mg/L}$  ;  $\text{CaSO}_4 = 0.34 \text{ mg/L}$  ;  $\text{MgCO}_3 = 0.42 \text{ mg/L}$  ;  
 $\text{MgCl}_2 = 0.76 \text{ mg/L}$  ;  $\text{MgSO}_4 = 0.90 \text{ mg/L}$  ;  $\text{NaCl} = 2.34 \text{ mg/L}$  and  $\text{SiO}_2 = 2.34 \text{ mg/L}$ .

[RGPV, May 2001, Dec. 2000]

**Solution.** NaCl and  $\text{SiO}_2$  do not require lime and soda.  $\text{CaCO}_3$  and  $\text{MgCO}_3$  impurities are considered as bicarbonates of calcium and magnesium respectively.

It is assumed that only the weights of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  have been expressed in terms of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . Thus, the lime requirement for  $\text{MgCO}_3$  is 2 equivalents as in the case of  $\text{Mg}(\text{HCO}_3)_2$  whereas for  $\text{CaCO}_3$ , lime requirement is only one equivalent. There is no soda requirement for either  $\text{CaCO}_3$  or  $\text{MgCO}_3$ .

## Lime requirement

$$\begin{aligned}
 &= \frac{74}{100} [\text{CaCO}_3 + 2 \times \text{MgCO}_3 + \text{MgCl}_2 + \text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}] \frac{\text{mg}}{\text{L}} \times (24,000 \times 365 \text{ L}) \\
 &\quad \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times \frac{100}{88.3} \\
 &= \frac{74}{100} \left[ 1.85 \times \frac{100}{100} + 2 \times 0.42 \times \frac{100}{84} + 0.76 \times \frac{100}{95} + 0.90 \times \frac{100}{120} \right] \times \frac{24,000 \times 365 \times 100}{10^6 \times 88.3} = 32.3 \text{ kg.}
 \end{aligned}$$

## Soda requirement

$$\begin{aligned}
 &= \frac{106}{100} [\text{CaSO}_4 + \text{MgCl}_2 + \text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}] \frac{\text{mg}}{\text{L}} \times (24,000 \times 365 \text{ L}) \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times \frac{100}{99.2} \\
 &= \frac{106}{100} \left[ 0.34 \times \frac{100}{136} + 0.76 \times \frac{100}{95} + 0.90 \times \frac{100}{120} \right] \times \frac{24,000 \times 365 \times 100}{10^6 \times 99.2} = 16.85 \text{ kg.}
 \end{aligned}$$

**Example 12.** Calculate the lime and soda required to soften 10,000 litres of hard water having the following analysis:  $\text{Ca}^{2+} = 250 \text{ ppm}$  as  $\text{CaCO}_3$  equivalents;  $\text{Mg}^{2+} = 100 \text{ ppm}$  as  $\text{CaCO}_3$  equivalents;  $\text{HCO}_3^-$  alkalinity = 300 as  $\text{CaCO}_3$  equivalents. [RGPV, June 2002]

## Solution. Lime requirement

$$\begin{aligned}
 &= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- \text{ as CaCO}_3 \text{ eq.}] \times \text{Volume of water} \\
 &= \frac{74}{100} [250 + 100] \text{ mg/L} \times 10,000 \text{ L} = 259 \times 10^4 \text{ mg} = 2.59 \text{ kg}
 \end{aligned}$$

## Soda requirement

$$\begin{aligned}
 &= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ as CaCO}_3 \text{ eq.}] \times \text{Volume of water} \\
 &= \frac{106}{100} [250 + 100 - 300] \text{ mg/L} \times 10,000 \text{ L} \\
 &= 53 \times 10^4 \text{ mg} = 0.53 \text{ kg.}
 \end{aligned}$$



**Example 13.** A turbid hard water, using  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  as a coagulant at the rate of 278 ppm, gave the following results on analysis :  $\text{Ca}(\text{HCO}_3)_2 = 162 \text{ ppm}$  ;  $\text{Mg}(\text{HCO}_3)_2 = 146 \text{ ppm}$  ;  $\text{MgSO}_4 = 120 \text{ ppm}$  ;  $\text{CaSO}_4 = 136 \text{ ppm}$  ;  $\text{CaCl}_2 = 111 \text{ ppm}$  ;  $\text{MgCl}_2 = 95 \text{ ppm}$ .

Calculate the temporary and permanent hardness of water. Also calculate lime and soda needed for softening 1,00,000 litres of the water sample. [RGPV, Dec. 2002]

**Solution.** (i) Temporary hardness =  $\text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2$

$$= 162 \times \frac{100}{162} + 146 \times \frac{100}{146} = 100 + 100 = 200 \text{ ppm.}$$

(ii) Permanent hardness =  $\text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2 + \text{MgCl}_2$

$$= 120 \times \frac{100}{120} + 136 \times \frac{100}{136} + 111 \times \frac{100}{111} + 95 \times \frac{100}{95} = 400 \text{ ppm.}$$

(iii) Lime requirement

$$= \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2 \text{Mg}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{MgSO}_4 + \text{FeSO}_4 \cdot 7 \text{H}_2\text{O} \text{ as CaCO}_3 \text{ equivalents}] \times \text{Volume of water}$$

$$= \frac{74}{100} \left[ 162 \times \frac{100}{162} + 2 \times 146 \times \frac{100}{146} + 95 \times \frac{100}{95} + 120 \times \frac{100}{120} + 278 \times \frac{100}{278} \right] \frac{\text{mg}}{\text{L}} \times 1,00,000 \text{ L}$$

$$= \frac{74}{100} [100 + 200 + 100 + 100 + 100] \times 10^5 \text{ mg}$$

$$= 74 \times 6 \times 10^5 \text{ mg} = 44.4 \times 10^6 \text{ mg} = 44.4 \text{ kg.}$$

(iv) Soda requirement

$$= \frac{106}{100} [\text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2 + \text{MgCl}_2 + \text{FeSO}_4 \cdot 7 \text{H}_2\text{O as CaCO}_3 \text{ eq.}] \times \text{Volume of water}$$

$$= \frac{106}{100} \left[ 120 \times \frac{100}{120} + 136 \times \frac{100}{136} + 111 \times \frac{100}{111} + 95 \times \frac{100}{95} + 278 \times \frac{100}{278} \right] \text{mg/L} \times 10^5 \text{ L}$$

$$= \frac{106}{100} [100 + 100 + 100 + 100 + 100] \times 10^5 \text{ mg}$$

$$= 106 \times 5 \times 10^5 \text{ mg} = 530 \times 10^6 \text{ mg} = 53 \text{ kg.}$$

**Example 14.** A water sample on analysis gave the following results :

- |   |  |
|---|--|
| (i) $\text{Ca}^{2+} = 30 \text{ mg/L,}$     | (ii) $\text{Mg}^{2+} = 18 \text{ mg/L,}$ |
| (iii) $\text{K}^+ = 19.5 \text{ mg/L,}$     | (iv) $\text{CO}_2 = 11 \text{ mg/L,}$    |
| (v) $\text{HCO}_3^- = 122 \text{ mg/L,}$    | (vi) $\text{Cl}^- = 35.5 \text{ mg/L,}$  |
| (vii) $\text{SO}_4^{2-} = 48 \text{ mg/L.}$ |  |

Calculate total hardness and alkalinity present in water sample. Also calculate lime soda required for softening one litre of this sample of hard water. [RGPV, June 2001]

**Solution.** Total hardness =  $[\text{Ca}^{2+} + \text{Mg}^{2+} + \text{HCO}_3^-]$

$$= \left[ 30 \times \frac{100}{40} + 18 \times \frac{100}{24} + 122 \times \frac{100}{122} \right] = 250 \text{ ppm}$$

$$\text{Alkalinity} = \text{HCO}_3^- = 122 \times \frac{100}{122} = 100 \text{ ppm}$$

Lime required

$$= \frac{74}{100} [\text{Mg}^{2+} + \text{CO}_2 + \text{HCO}_3^- \text{ all as CaCO}_3 \text{ equivalents}] \text{ mg/L} \times V \text{ (L)}$$

$$= \frac{74}{100} \left[ 18 \times \frac{100}{24} + 11 \times \frac{100}{44} + 122 \times \frac{100}{122} \right] \text{ mg/L} \times V \text{ (L)}$$

$$= 148 \text{ mg/L} \times 1 \text{ (L)} = 148 \text{ mg}$$

Soda required

$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ all as CaCO}_3 \text{ equivalents}] \text{ mg/L} \times V \text{ (L)}$$

$$= \frac{106}{100} \left[ 30 \times \frac{100}{40} + 18 \times \frac{100}{24} - 122 \times \frac{100}{122} \right] \text{ mg/L} \times 1 \text{ (L)}$$

$$= 53 \text{ mg}$$

**Example 15.** A water sample, using  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  as a coagulant at the rate of 139 ppm, gave the following results for raw water :  $\text{Ca}^{2+} = 320 \text{ ppm}$  ;  $\text{Mg}^{2+} = 120 \text{ ppm}$  ;  $\text{CO}_2 = 88 \text{ ppm}$  ;  $\text{HCO}_3^- = 732 \text{ ppm}$ . Calculate lime and soda required for softening of 1000 litres of raw water.

[RGPV June 2003]

**Solution.** Lime

$$= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{FeSO}_4 \cdot 7 \text{H}_2\text{O as CaCO}_3 \text{ eq.}] \text{ mg/L}$$

$$= \frac{74}{100} \left[ 120 \times \frac{100}{24} + 732 \times \frac{100}{122} + 88 \times \frac{100}{44} + 139 \times \frac{100}{278} \right] \text{ mg/L}$$

$$= 999 \text{ mg/L.}$$

Now, lime required for softening 1000 L of raw water

$$= 999 \text{ mg/L} \times 1000 \text{ L}$$

$$= 999 \times 10^3 \text{ mg} = 999 \text{ gm.}$$

$$\text{Soda} = \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- + \text{FeSO}_4 \cdot 7 \text{H}_2\text{O as CaCO}_3 \text{ eq.}] \text{ mg/L}$$

$$= \frac{106}{100} \left[ 320 \times \frac{100}{40} + 120 \times \frac{100}{24} - 732 \times \frac{100}{122} + 139 \times \frac{100}{278} \right] \text{ mg/L}$$

$$= 795 \text{ mg/L.}$$

Now soda required for softening 1000 L of raw water

$$= 795 \text{ mg/L} \times 1000 \text{ L}$$

$$= 795 \times 10^3 \text{ mg} = 795 \text{ gm.}$$



### 11.2 Zeolite or Permutit Process

**Zeolites** are naturally occurring hydrated sodium aluminosilicate minerals (like  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2\text{O}$  where  $x = 2 - 10$  &  $y = 2 - 6$ ) capable of exchanging reversibly its sodium ions for hardness-producing ions in water.

Zeolites are also known as *permutits* and in Greek it means 'boiling stone'.

A zeolite crystal can be considered to result from the linking of several  $\text{SiO}_4$  tetrahedra, each oxygen of a tetrahedron being shared with an adjacent one. The empirical formula is thus  $(\text{SiO}_2)_n$ . However, some of the  $\text{Si}^{4+}$  ions may be isomorphously replaced by  $\text{Al}^{3+}$  ions and in order to balance the charges an extra positive-ion such as  $\text{Na}^+$  and  $\text{K}^+$  must also be incorporated for every  $\text{Al}^{3+}$  introduced. The linking of these tetrahedra results in an open structure with cavities. The porous nature of the structure permits free movement of water molecules and ions.

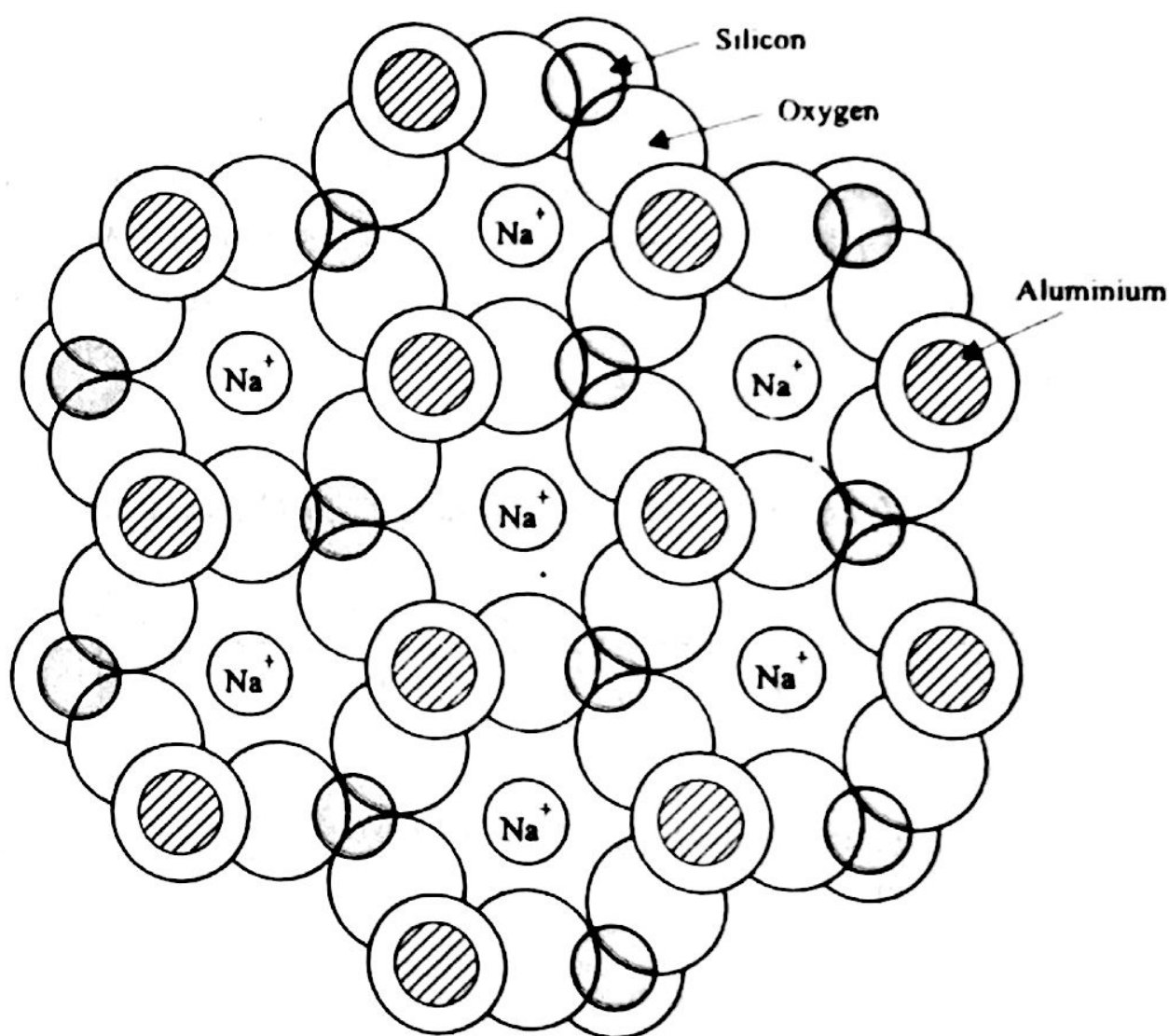


Fig. 12. Structure of a naturally occurring zeolite,  $\text{NaAlSiO}_4$ . The sodium ions are loosely held in holes in the lattice.

Zeolites are of two *types viz.* natural and synthetic.

(i) *Natural zeolites* are non-porous, amorphous and durable for example, natrolite,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

(ii) *Synthetic zeolites* are porous and possess a gel structure. They are prepared by heating together sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ).

Synthetic zeolites possess higher exchange capacity per unit weight compared to natural zeolites.

**Process.** For softening of water by zeolite process, hard water is percolated at specified rate through a bed of zeolite, housed in a cylindrical unit, see Fig. 13.

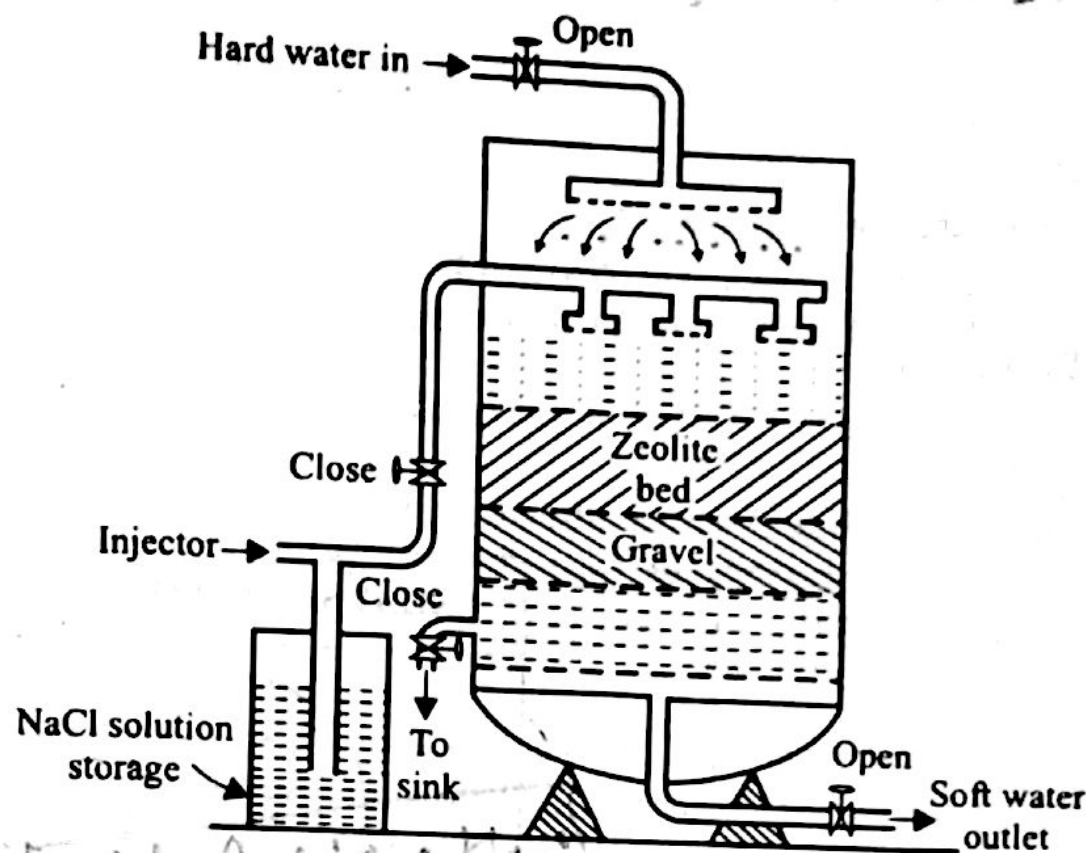
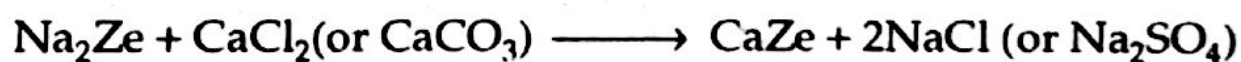
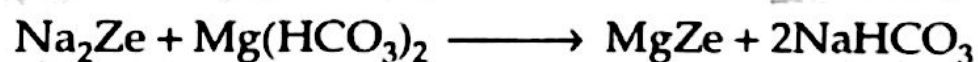


Fig. 13. Zeolite softener.

Zeolite holds sodium ions loosely and can be simply represented as  $\text{Na}_2\text{Ze}$  where Ze represents insoluble radical frame work.

The hardness-causing ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc.) are retained by the zeolite as  $\text{CaZe}$  and  $\text{MgZe}$  respectively, while the outgoing water contains sodium salts. In the process, the water becomes free from  $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$ , the main hardness producing cations.

Reactions taking place during the softening process are :



**Regeneration.** After some time, the zeolite is completely converted into calcium and magnesium zeolites. Eventually, the bed ceases to soften water, i.e., it gets exhausted. At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated sodium chloride (brine) solution when the following reactions take place.



Exhausted zeolite

Brine

Reclaimed zeolite

Washings

The washings (containing  $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) are led to drain and the regenerated zeolite bed thus obtained is used again for softening purpose. [Instead of  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$  etc. can also be used for regeneration but  $\text{NaCl}$  is mostly used because of its low cost and the products of regeneration process ( $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) are highly soluble and can be easily rinsed out from the zeolite bed].



The working of zeolite softeners involve alternate cycles of softening run and the regeneration run. The scheme for softening processes are represented in Fig. 14 below :

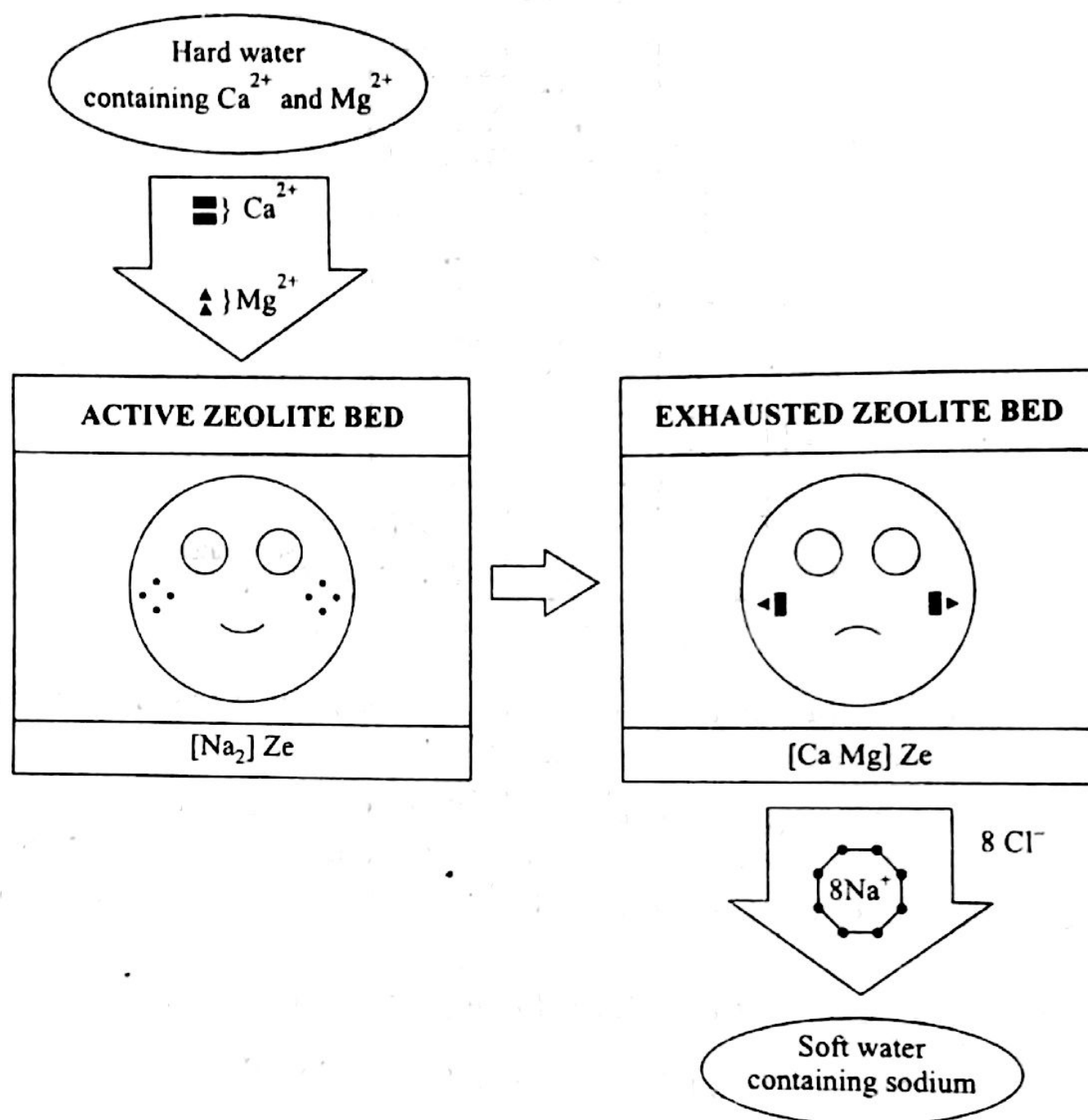
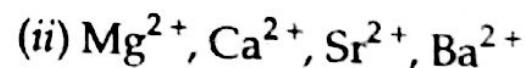


Fig. 14. Illustration of the water softening process using zeolite.

Arrange the following exchanging ions in increasing order of extent of exchange with the  $\text{Na}^+$  ions of the zeolite.



Ans. (i)  $\text{Ca}^{2+} < \text{Al}^{3+} < \text{Th}^{4+}$

(ii)  $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$

#### Limitations of zeolite process

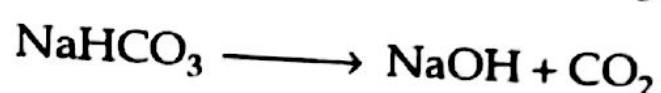
(1) If the supplied water is turbid, the suspended matter must be removed (by coagulation, filtration, etc.) before the water is fed to the zeolite bed. Otherwise the pores of the zeolite bed will get clogged by the turbidity, thereby making it inactive.

(2) If water contains large quantities of  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ , they must be removed first because these ions produce manganese and iron zeolites, which are very difficult to be regenerated.

(3) Mineral acids, if present in water, destroy the zeolite bed and hence they must be neutralized with soda in advance, before feeding the water into the zeolite bed.

(4) The water to be softened should not be hot as the zeolite tends to dissolve in it.

(5) Anions are not removed by this process. Thus the bicarbonates present in hard water get converted to  $\text{NaHCO}_3$  which goes into soft water effluent. If it is used as boiler feed, under the boiler conditions  $\text{NaHCO}_3$  dissociates to



Both the products are not desirable. Since  $\text{NaOH}$  may lead to caustic embrittlement and  $\text{CO}_2$  makes the condensed water acidic and corrosive. Thus it is desirable to remove temporary hardness before subjecting the raw water to zeolite process.

(6) Compared to ion-exchange process, water treated by the zeolite process contains 25% more dissolved solids. Moreover, the higher cost of the plant and materials are also limiting factors.

#### Advantages of zeolite process

- (i) The hardness is nearly completely removed and water of about 10 ppm hardness is produced.
- (ii) The equipment used is compact and occupies less space.
- (iii) It is quite clean and rapid process which requires less time for softening.
- (iv) For maintenance as well as operations, less skill is needed.
- (v) Impurities are not precipitated, so there is no danger of sludge formation.
- (vi) The process automatically adjusts itself to waters of different hardness.

#### SOLVED EXAMPLES

**Example 1.** The hardness of 10,000 litres of a sample of water was removed by passing it through a zeolite softener. The zeolite softener then required 200 litres of sodium chloride solution containing 150 gm/litre of  $\text{NaCl}$  for regeneration. Find the hardness of water sample.

**Solution.**  $\text{NaCl}$  contained in 200 L of  $\text{NaCl}$  solution

$$= 150 \text{ gm/L} \times 200 \text{ L}$$

$$= 30,000 \text{ gm of NaCl} = 30,000 \times \frac{50}{58.5}$$

$$= 25,641 \text{ gm equivalents of CaCO}_3$$

$$\therefore 10,000 \text{ litres of water} = 25,641 \text{ gm equivalents of CaCO}_3$$

$$\Rightarrow 1 \text{ L of water} = \frac{2.564 \times 10^7}{10,000} \text{ mg/L of CaCO}_3 \text{ eq.}$$

Hence, hardness of water is 2564 ppm.



**Example 2.** An exhausted zeolite softener was regenerated by passing 200 litres of NaCl solution, having a strength of 0.2 gm/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 350 clark.

[RGPV, Dec. 2003]

**Solution.** 200 L of NaCl solution contains =  $200 \text{ L} \times (0.2 \text{ g/L})$  of NaCl

$$= 40 \text{ gm of NaCl}$$

$$= 40 \text{ gm} \times \left( \frac{100}{117} \right) \text{ CaCO}_3 \text{ eq.}$$

$$= 34.188 \text{ gm CaCO}_3 \text{ eq.}$$

$$= 34188 \text{ mg CaCO}_3 \text{ eq.}$$

$$\text{Let } V \text{ litres of } 350^\circ \text{Cl} = \frac{350}{0.07} \text{ ppm}$$

$$= 5000 \text{ ppm (or } 5000 \text{ gm/L) water contains hardness}$$

$$= 34188 \text{ mg CaCO}_3 \text{ eq.}$$

$$\therefore \text{ Number of litres of hard water, } V = \frac{34188}{5000} = 6.84 \text{ L.}$$

**Example 3.** A zeolite softener was 90% exhausted by removing the hardness completely when 10,000 litres of hard water sample passed through it. The exhausted zeolite bed required 200 litres of 3% sodium chloride solution for its complete regeneration. Calculate the hardness of water solution.

[RGPV, Dec. 2002]

**Solution.** NaCl contained in 200 L of 3% NaCl solution

$$= 30 \text{ gm/L} \times 200 \text{ L}$$

$$= 6,000 \text{ g NaCl}$$

$$= 6,000 \times \frac{50}{58.5}$$

$$= 5,128 \text{ gm equivalents of CaCO}_3$$

$$\therefore 90\% \text{ hardness of } 10,000 \text{ L of water} = 5,128 \text{ gm equivalents CaCO}_3$$

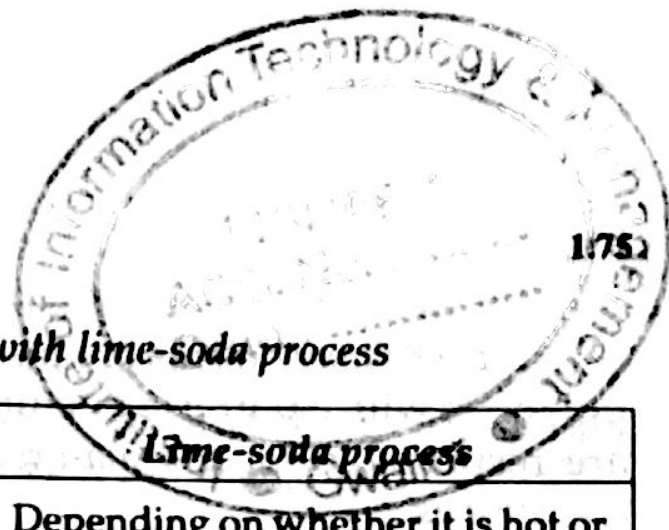
$$\Rightarrow 1 \text{ L of water} = \frac{5,128}{\left( 10,000 \times \frac{90}{100} \right)} = \frac{5,128}{9000}$$

$$= 0.5698 \text{ gm equivalents of CaCO}_3$$

$$= 0.5698 \times 1000 \text{ mg CaCO}_3 \text{ eq.}$$

$$= 569.8 \text{ mg CaCO}_3 \text{ eq.}$$

Hence, hardness of water is 569.8 mg/L or 569.8 ppm.

**Table 9 : Comparison of Zeolite process with lime-soda process**

Characteristic	Zeolite process	Lime-soda process
1. Residual hardness	This process produces water of 10-15 ppm residual hardness.	Depending on whether it is hot or cold process, water of, generally, 15-50 ppm hardness is obtained.
2. Dissolved solids	Water treated with zeolite process contains larger amount of sodium salts than in original raw water.	Treated-water contains lesser % of sodium salts.
3. Capital cost	The cost of plant and zeolite are higher. Hence the capital cost is higher.	The capital cost is lower.
4. Operating expenses	Operation expenses are lower as cheap NaCl is required for regeneration.	Operation expenses are higher as costly chemicals (lime, soda and coagulant) are consumed.
5. pH of raw water	It cannot be used for treating acidic water, because the zeolite material undergoes disintegration.	There is no such limitation.
6. Plant size	The plant occupies less space as it is compact.	Plant occupies more space, as it depends on the amount of water to be softened.
7. Raw water pre-treatment	The raw water to be softened must be free from suspended matter ; otherwise the pores of zeolite material are blocked and the bed loses its exchange capacity.	The process is free from such limitation.
8. Operation	It can operate under pressure and can be designed for fully automatic operation.	This process cannot be operated under pressure.
9. Sludge trouble	It involves no problem of settling, coagulation, filtration and removal of the sludges and precipitates.	It involves difficulty in settling, coagulation, filtration and removal of precipitates.
10. Supervision	Control test comprises only in checking the hardness of treated water. The process adjusts itself to water of different hardness.	In order to meet the changing hardness of incoming water, frequent control and adjustments of reagents is needed.
11. Results	Treated-water contains more $\text{NaHCO}_3$ which creates problem when used as feed water in boilers.	Treated-water is completely free from $\text{NaHCO}_3$ because it is removed in the form of insoluble $\text{CaCO}_3$ and $\text{Mg(OH)}_2$ .

**11.3 Demineralization or Deionization by Ion-exchange Process**

Ion exchange is a process by which ions held on a porous, essentially insoluble solid are exchanged for ions in solution that is brought in contact with it.



**Ion-exchange resins** are insoluble, cross-linked, high molecular weight, organic polymers with a porous structure, and the "functional groups" attached to the chains are responsible for the ion-exchange properties. The ion-exchange resins may be classified as :

(i) **Cation exchange resins ( $R^-H^+$ )** : They are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water (Fig. 15).

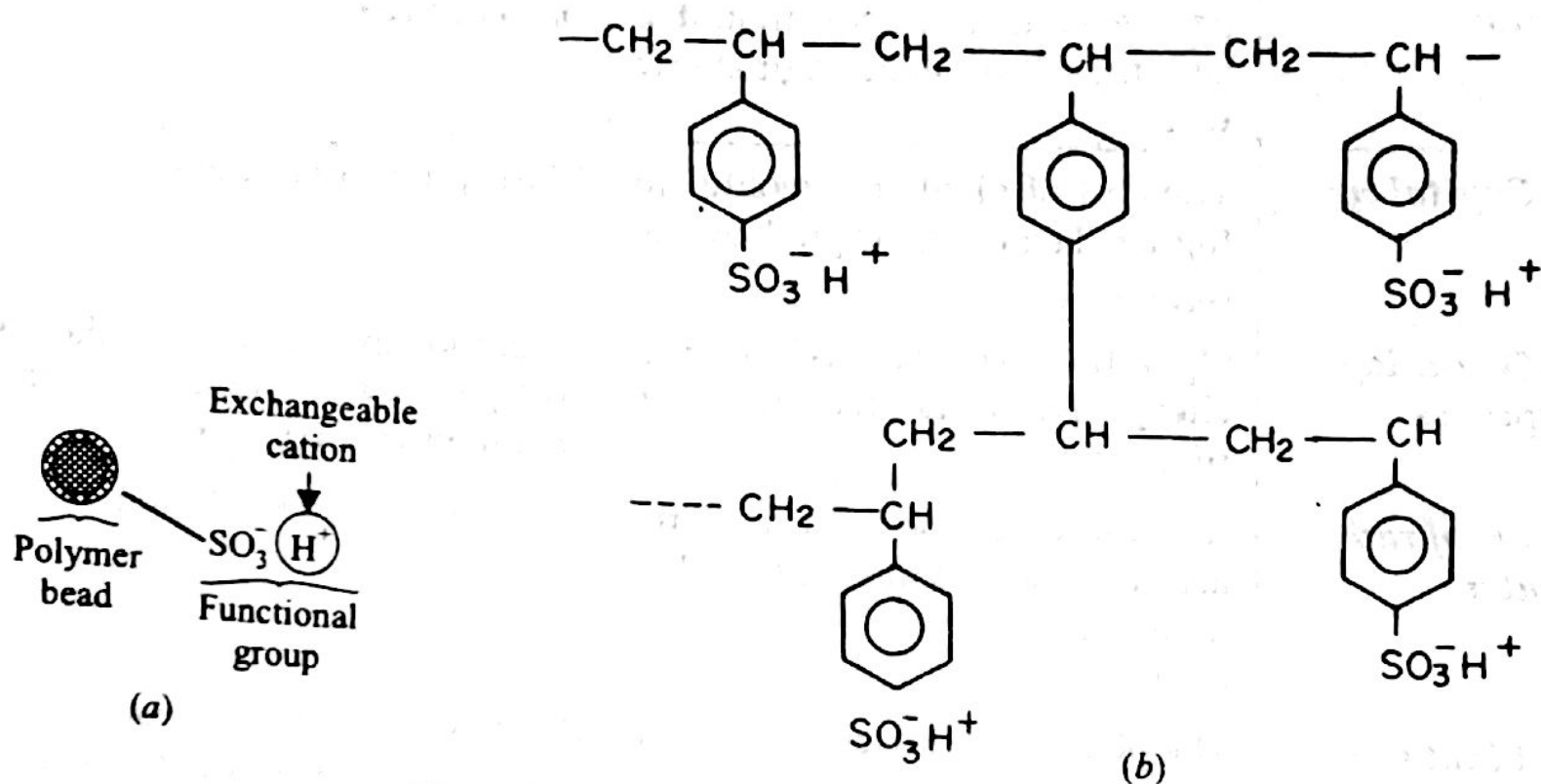


Fig. 15. Sulphonate form of cation-exchanger.

Such resins have acidic functional groups like  $-SO_3H$ ,  $-COOH$  or  $-OH$  (phenolic) capable of exchanging the cationic portion of minerals by their hydrogen ions, and hence they are termed as cation exchangers.

Amberlite IR-120 and Dowex-50 are examples of commercially available cation exchange resins.

(ii) **Anion exchange resins ( $R^+OH^-$ )** : They are styrene-divinyl benzene or amine formaldehyde copolymers, which contain basic functional groups such as

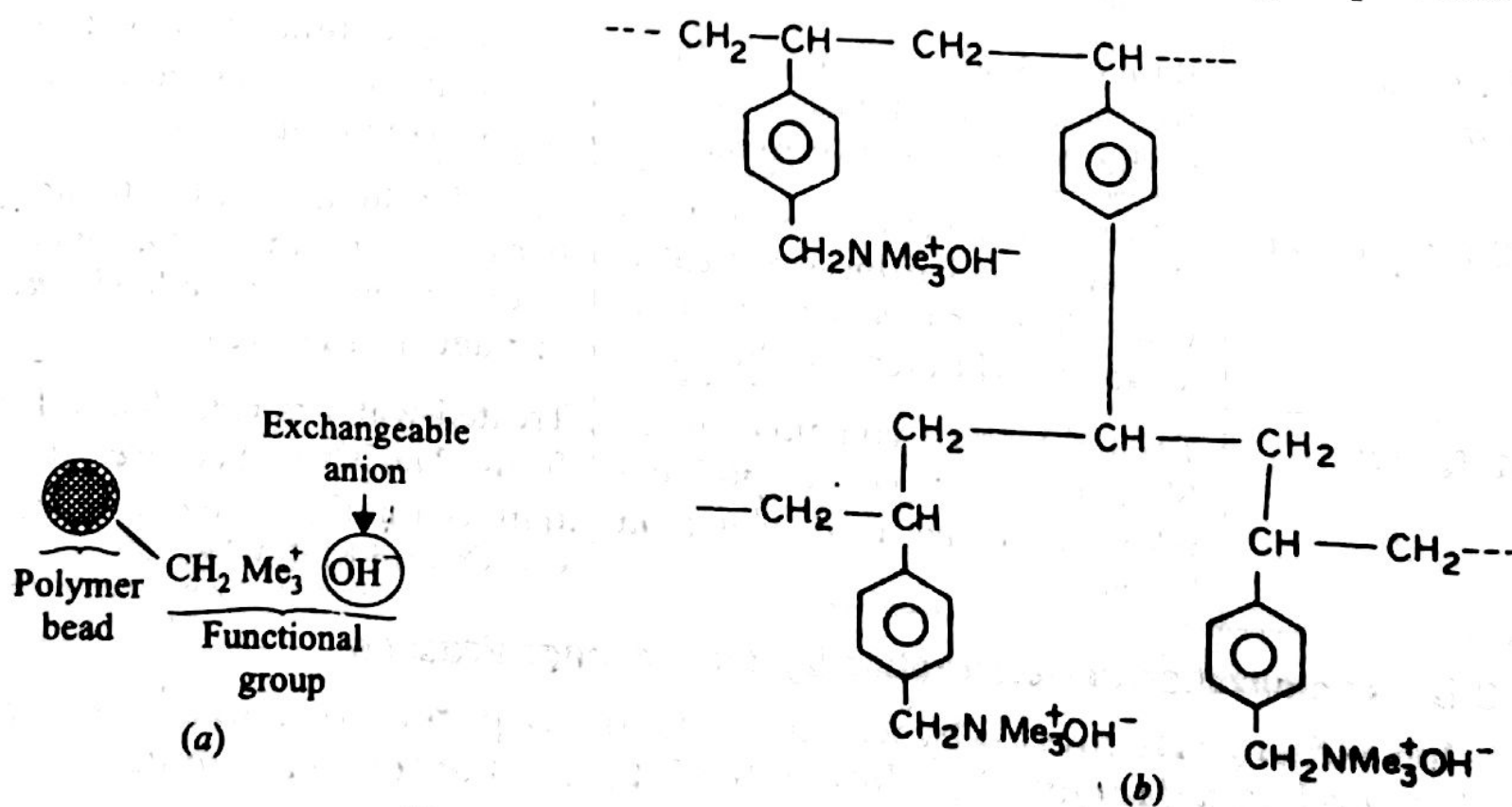


Fig. 16. Hydroxide form of anion-exchanger.

amino or quaternary ammonium ( $-N^+R_3$ ) or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix (Fig. 16). These, after treatment with dil. NaOH solution, become capable to exchange their  $OH^-$  anions with anions in water and therefore they are known as anion exchangers.

Ambertite-400 and Dowex-3 are examples of commercially available anions exchange resins.

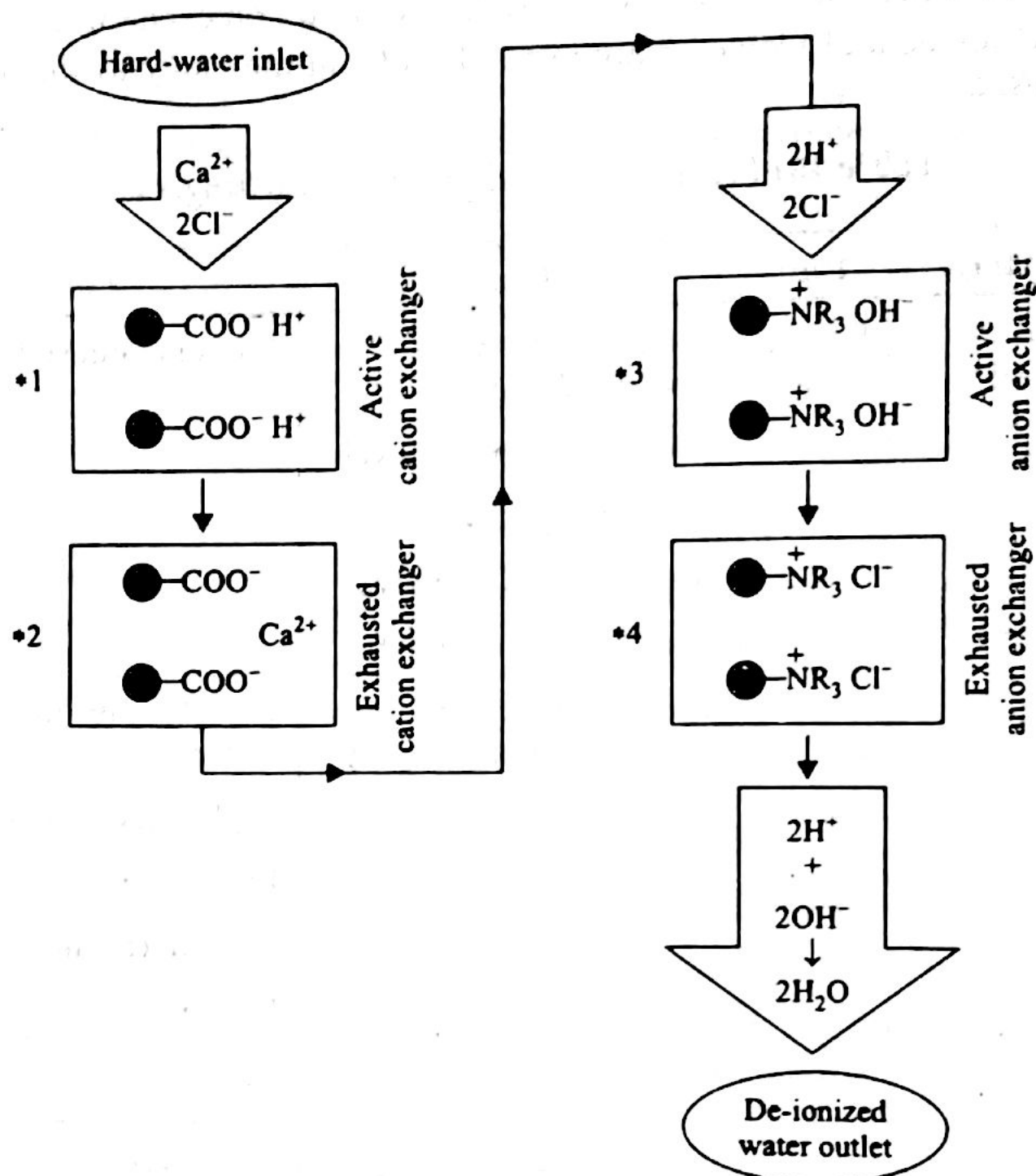
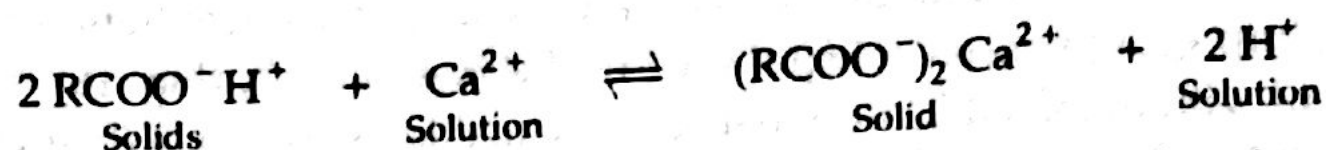
**Table 10 : Pros and cons of different Ion-exchangers**

	Exchanger	Type	Pros	Cons
1.	Cation exchanger	Strong acid	Useful for any water, Low initial cost, Complete cation removal, Variable capacity, Good physical stability, Good oxidation stability	Low operating efficiency
		Weak acid	Very high capacity High operating efficiency	Useful only for specific water, High initial cost, Partial cation removal, Fixed operating capacity, Poor physical stability,
2.	Anion exchanger	Strong base	Low initial cost, Complete anion removal Variable capacity	Less resistance to organic fouling, Limited life, Thermodynamically unstable, Efficiency or quality,
		Weak base	High operating capacity Excellent resistance to organic fouling Good thermal and oxidation stability	High initial cost, Partial anion removal Does not remove silica or $CO_2$

**Process.** The hard water is first passed through cation exchange column Fig. 17, when all the cations like  $Ca^{2+}$ ,  $Mg^{2+}$ , etc. are removed (taken up by the resin) from it, and equivalent amount of  $H^+$  ions are released from this column to water.



Thus



- \*1. Styrene-divinyl benzene copolymer after functionalization with carboxylic acid groups becomes cation exchange resin with exchangeable  $\text{H}^+$  ions.
- \*2. The  $\text{Ca}^{2+}$  ions from the hard water replace the  $\text{H}^+$  ions in the cation-exchanger, and de-cationized water is obtained.
- \*3. Styrene-divinyl benzene copolymer after functionalization with quaternary ammonium hydroxide becomes anion exchange resin with exchangeable  $\text{OH}^-$  ions.
- \*4. The  $\text{Cl}^-$  ions from the de-cationized water replace the  $\text{OH}^-$  ions in the anion-exchanger.

Fig. 17. Illustration of the de-ionization process using ion-exchange resins.

After passing through cation exchange column, the hard water is passed through anion exchange column, when all the anions like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , etc. present in the water are removed (taken up by resin) and equivalent amount of  $\text{OH}^-$  ions are released from this column to water. Thus :



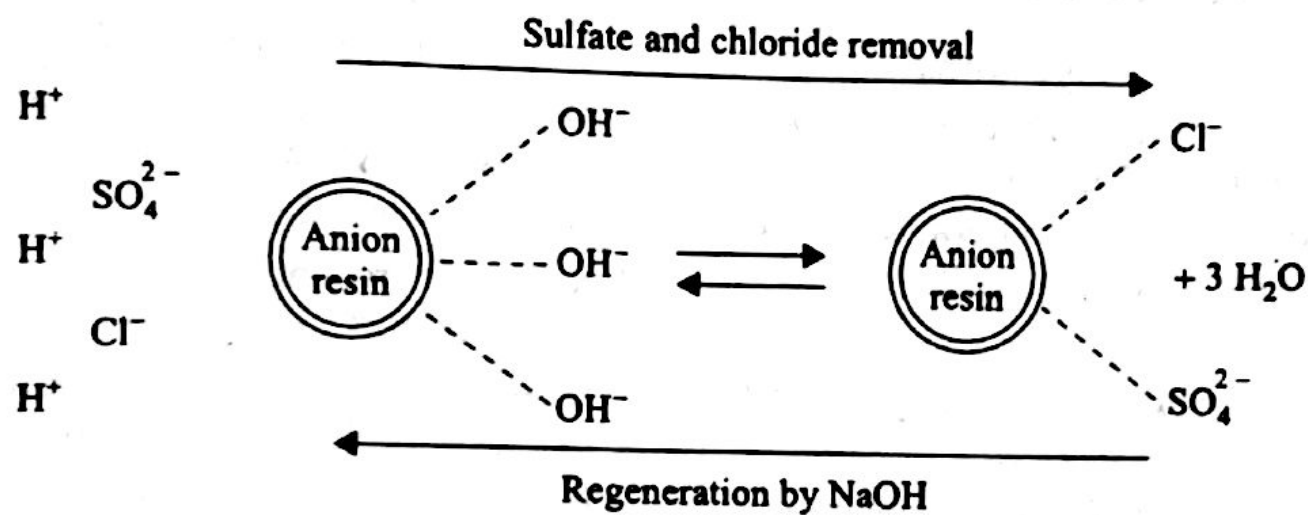
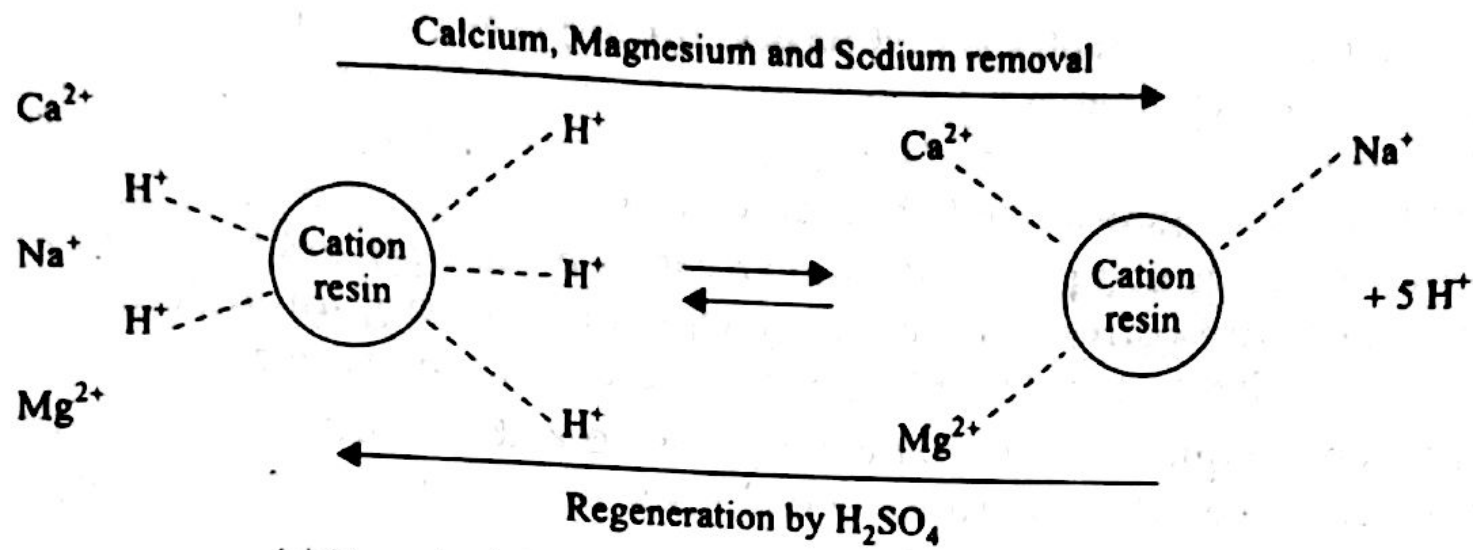
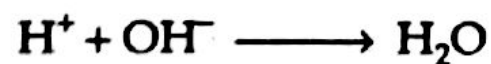
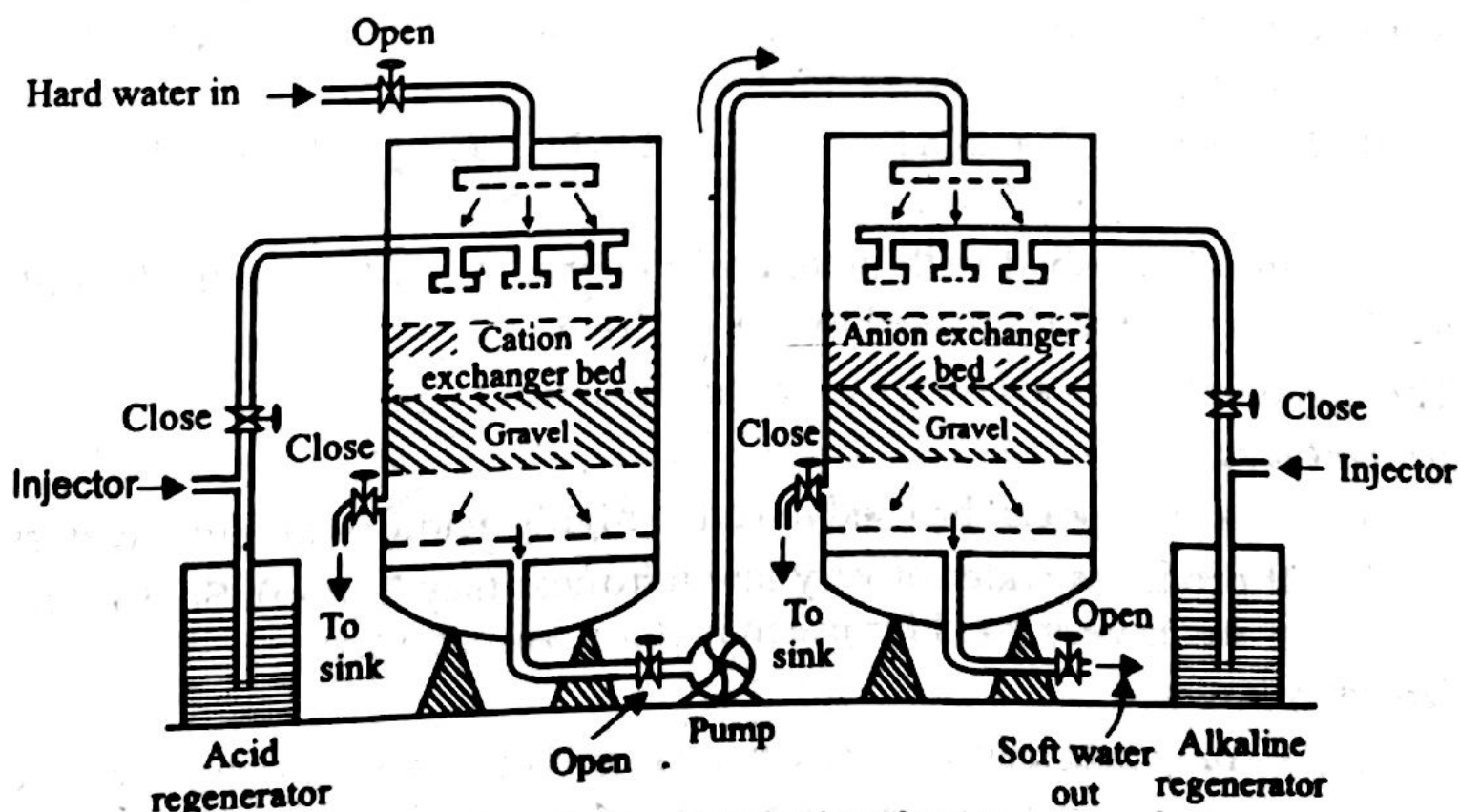


Fig. 18. Principles of ion-exchange processes.

$\text{H}^+$  and  $\text{OH}^-$  ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.



Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water, is known as *deionized* or *demineralized water*, and is also free from acidity or alkalinity. Thus it is as pure as distilled water.





For deionization, water is first passed through the cation exchanger and then through the anion exchanger.

This is because cation exchangers are easily attacked by alkalis, whereas all types of ion-exchangers are not attacked by acids.

When water is first passed through a cation exchanger, salts present in water are converted into corresponding acids, which on passing through an anion exchanger do not harm it and finally get converted into pure water.

If reverse sequence is used, then on passing water through anion-exchanger, alkali is produced which harms the cation-exchanger in subsequent step. Thus, such a sequence is usually avoided.

#### Differences between soft water and demineralised water :

	Soft Water	Demineralised Water
1.	Soft water has hardness $\leq 85$ ppm ( $\text{CaCO}_3$ eq.). Thus, soft water has more hardness than demineralised water.	Demineralised water does not have any salt (or cations & anions) present in it. So, hardness $\leq 2$ ppm.
2.	It is fit for domestic use.	It is not recommended as such for drinking purposes.
3.	It can be made by using either Lime-Soda process or Zeolite process.	It can be made either by distillation or by using cation & anion exchangers.
4.	Soft water is unfit for feeding into boilers.	It is very good for use in high-pressure boilers.

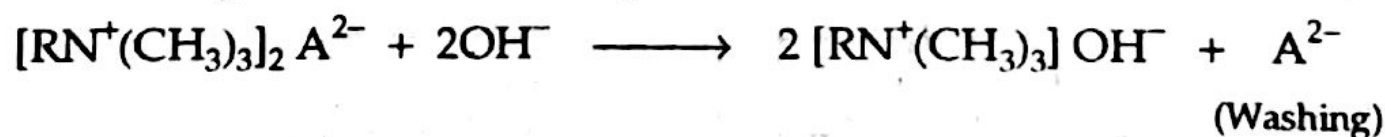
**Regeneration.** When capacities of cation and anion exchangers to exchange  $\text{H}^+$  and  $\text{OH}^-$  ions respectively are lost, they are then said to be *exhausted*.

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil.  $\text{H}_2\text{SO}_4$ . The regeneration can be represented as :



The column is washed with deionized water and washing (which contains  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc. and  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  ions) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as :



The column is washed with deionized water and washing (which contains  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  ions) is passed to sink or drain.

The regenerated ion exchange resins are then used again.

#### Advantages

- (i) The process can be used to soften highly acidic or alkaline waters.
- (ii) It produces water of very low hardness (say 2 ppm). So, the treated water is very good for use in high pressure boilers.

#### Disadvantages

- (i) Capital cost is high since chemical and equipment both are costly.
- (ii) If water contains turbidity then the efficiency of the process is reduced.

**Example 1.** After treating  $10^4$  L of water by ion exchanger, the cationic resin required 200 L of 0.1 N HCl and anionic resin required 200 L of 0.1 N NaOH solutions. Find the hardness of the above sample of water.

**Solution.** We know that all hardness causing cations is removed by cation exchanger. Moreover, anions of the constituents present in water are removed by anion exchanger. Thus, the amount of acid used for regeneration of the cation resin refers hardness present.

Given Normality of HCl =  $N_1 = 0.1$  N

Volume of HCl =  $V_1 = 200$  L

Volume of hard water =  $V_2 = 10^4$  L

Let Normality of hard water =  $N_2$

Applying the Normality equation,

$$N_1 V_1 = N_2 V_2$$

$$\Rightarrow 0.1 \text{ N} \times 200 \text{ L} = N_2 \times 10^4 \text{ L}$$

$$\Rightarrow N_2 = 20 \times 10^{-4} \text{ L}$$

As equivalent weight of  $\text{CaCO}_3 = 50$

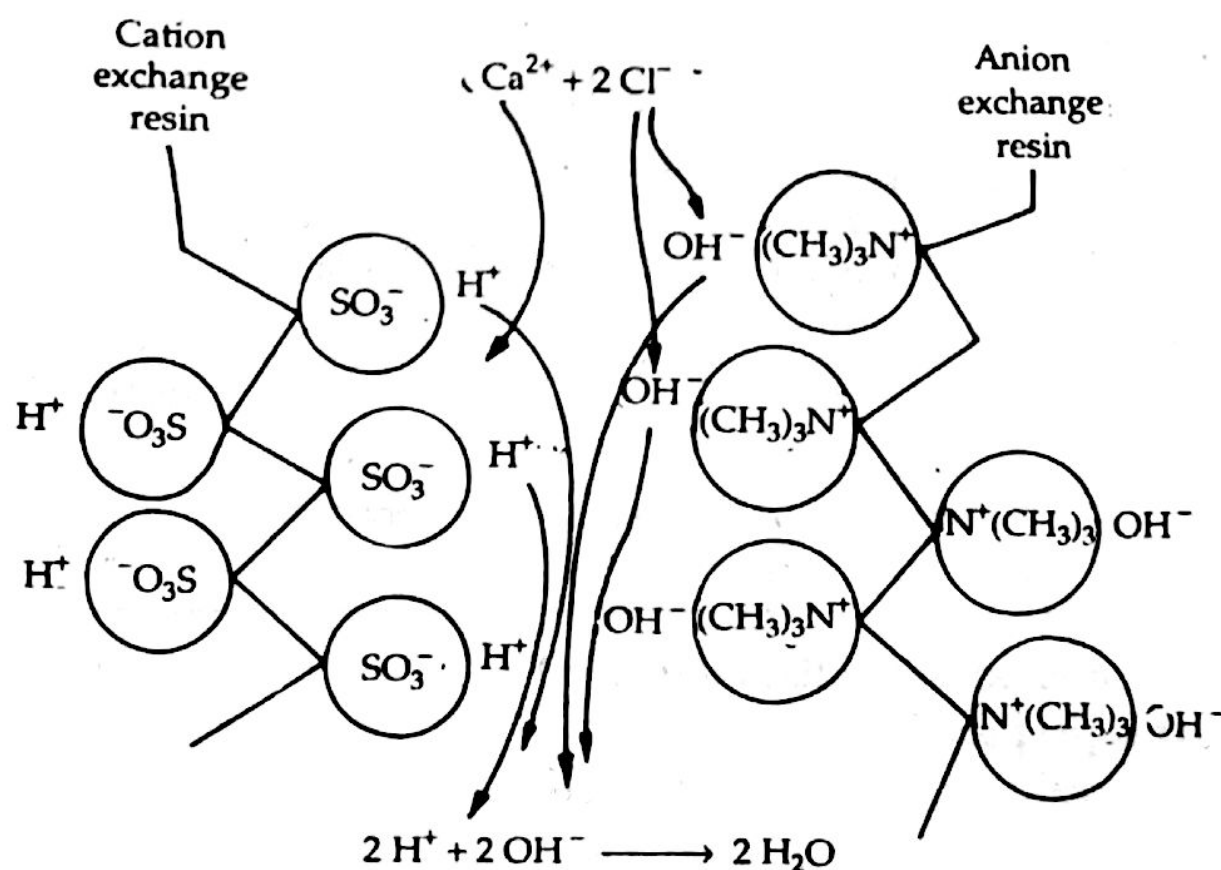
$\therefore$  Strength of hardness (expressed in terms of  $\text{CaCO}_3$  equivalent)

$$= N_2 \times 50 = (20 \times 10^{-4}) \times 50 \text{ g/L} = 0.1 \text{ g/L}$$

$$= 0.1 \times 1000 \text{ mg/L} = 100 \text{ mg/L}$$

$$\Rightarrow \text{Hardness} = 100 \text{ ppm.}$$

**Mixed bed deioniser.** This consists of a single cylinder containing an intimate mixture of strongly acidic cation exchanger and strongly basic anion exchanger.



**Fig. 20.** Deionization of a salt solution using a mixture of cation and anion-exchange resins. The zigzag lines represent the organic polymer matrix of the resin (most often a styrene-divinylbenzene copolymer), to which the sulfonate ( $-\text{SO}_3^-$ ) and quaternary ammonium ( $-\text{N}^+(\text{CH}_3)_3$ ) groups are chemically bonded.



Originally the cation exchanger is in the  $H^+$  form, and the anion exchanger is in the  $OH^-$  form. When hard water containing say  $CaCl_2$  is poured into the mixed resin bed from the top. Pure water flows out at the bottom. Each  $Ca^{2+}$  ion displaces two  $H^+$  ions and each  $Cl^-$  displaces one  $OH^-$  ions. Exactly equal numbers of  $H^+$  and  $OH^-$  are produced, which combine to form water, see Fig. 20.

**Regeneration.** To regenerate a mixed bed deioniser, it is first necessary to separate the two resins. They are then regenerated separately. The cation exchanger is regenerated by treatment with strong acid like  $H_2SO_4$  and the anion exchanger is regenerated by treatment with a strong base like  $NaOH$ .

Thus, it might be obvious that mixed bed deionisers are comparatively more convenient to use and are more efficient. But they are more costly too. In many areas, deionization is a simpler and less costly alternative to distillation and is widely used for purifying water used in chemical laboratories.

In domestic water softening by ion exchange, total deionization is not necessary. Only the cations responsible for water hardness need to be removed. So, only a cation-exchanger in  $Na^+$  form is used. Its operation is reversible and regeneration is carried out using readily available, inexpensive  $NaCl$  solution (brine).

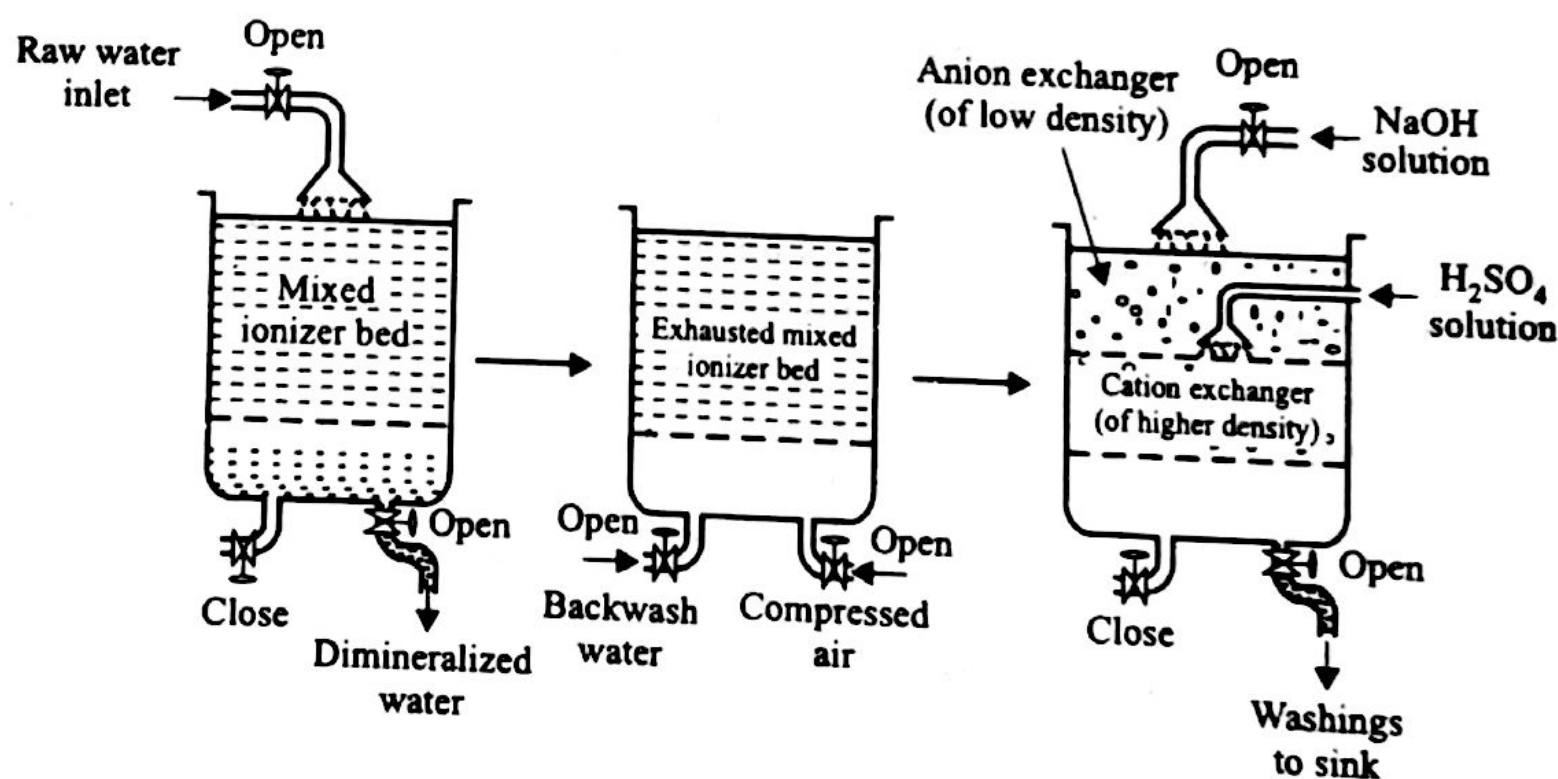


Fig. 21. Regeneration of mixed-bed ion exchanger.

- ☛ (a) What is intrinsic or polished water ?  
 (b) How it is prepared ?  
 (c) Why it should be immediately used ?

**Ans. (a)** Intrinsic or polished water is extremely pure water used for washing in the electronic equipment manufacturing processes like manufacture of TV tubes, transistors, etc.

(b) **Preparation of polished water.** First water is passed through columns of cation and anion exchangers and is again passed through a bed of mixed exchange-resins.

(c) As and when required, polished water is made and immediately used to avoid contamination.

☛ **What is cold lime-ion exchange process ?**

**Ans.** It is water softening process in which hard water is first treated with lime to economically remove the carbonate hardness. Then non carbonate hardness is removed by cation exchange.

**Advantages.** (i) Silica content is reduced without resorting to demineralization. (ii) Complete water softening.

☛ **What is hot lime-ion exchange softening ?**

**Ans.** In this process, the effluent from the hot L - S process is passed through sulphonated styrene resin based ion-exchangers (as they can withstand  $T \geq 100^\circ\text{C}$ ).

**Advantages.** Considerable decrease in the hardness of water and the silica content.

The Pros and Cons of ion-exchange, zeolite and lime-soda processes are summarized in Table 11.

**Table 11 : Comparison of Ion-exchange, Zeolite and lime-soda process**

S.no.	Characteristic	Ion-exchange process	Zeolite process	Lime-soda process
1.	Requirements	Cation and anion exchangers	zeolite	Lime, soda and coagulants
2.	Exchange of ions	Exchange of both cations and anions takes place	Exchange of only cations takes place	No exchange of ions.
3.	Capital cost	Very high	High	Low
4.	Operating expenses	High	Low	High
5.	Raw water	(i) Should be non-turbid (ii) Both acidic or alkaline water can be treated (iii) Prior knowledge of hardness not required	(i) Should be non-turbid (ii) Should not be acidic (iii) Prior knowledge of hardness not required.	Prior knowledge of hardness is essential
6.	Automation	Possible	Possible	Not possible
7.	Residual hardness	Least (0-2ppm)	Low (0-15 ppm)	High (15-50 ppm)



## 12 INTERNAL TREATMENT

It means treating the raw water inside the boiler. In this process (also called sequestration), an ion is prohibited to exhibit its original character by 'complexing' or converting it into other more soluble salt by adding appropriate reagent. It can be done by two processes : (a) In the first method, appropriate chemicals are added to the boiler water to precipitate the scale forming impurities in the form of 'sludges', which can be removed by blow-down operation, (b) In the second method, problem causing cations are converted into compounds, which will stay in "dissolved form" in water and thus do not cause any harm.

Internal treatment methods are, generally, followed by 'blow-down operations', so that accumulated sludge is removed. Some of the important internal treatment methods are briefly discussed below :

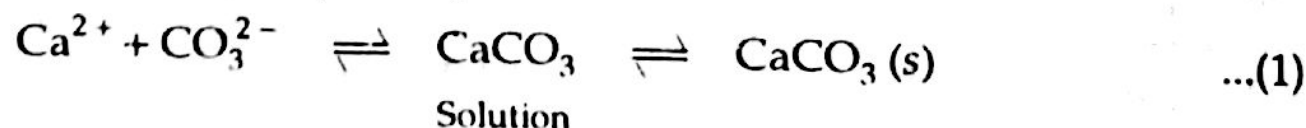
### 12.1 Colloidal conditioning

Scale formation can be avoided in low pressure boilers by adding substances like kerosene, tannin, agar-agar, etc. which get adsorbed over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by blow-down operation.

### 12.2 Carbonate conditioning

For a salt to be precipitated, the ions constituting the salt must be present in sufficient concentration so that the product of their concentrations (*i.e.*, ionic product) exceeds a limiting value known as the solubility product. Thus, for a salt like  $\text{CaCO}_3$  to be precipitated, the product of the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  must exceed the solubility product of  $\text{CaCO}_3$ , represented as  $K_{\text{SP}}^{\text{CaCO}_3}$ .

The formation of  $\text{CaCO}_3$  may be represented as



At any given temperature, when the equilibrium is established,

$$\underset{\substack{\text{Solubility product} \\ \text{of } \text{CaCO}_3}}{K_{\text{CaCO}_3}^{\text{SP}}} = \underset{\substack{\text{Concentration} \\ \text{of } \text{Ca}^{2+}}}{[\text{Ca}^{2+}]} \times \underset{\substack{\text{Concentration} \\ \text{of } \text{CO}_3^{2-}}}{[\text{CO}_3^{2-}]}$$

Under these conditions, if some sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is added, the concentration of  $\text{CO}_3^{2-}$  increases. In order to maintain the solubility product of  $\text{CaCO}_3$  constant, some  $\text{Ca}^{2+}$  will get precipitated.

Now, in a saturated calcium sulphate solution,



and

$$\underset{\substack{\text{Solubility product} \\ \text{of } \text{CaSO}_4}}{K_{\text{CaSO}_4}^{\text{SP}}} = \underset{\substack{\text{Concentration} \\ \text{of } \text{Ca}^{2+}}}{[\text{Ca}^{2+}]} \times \underset{\substack{\text{Concentration} \\ \text{of } \text{SO}_4^{2-}}}{[\text{SO}_4^{2-}]}$$

Now, in boiler water conditions, a solution is saturated w.r.t. both  $\text{CaCO}_3$  and  $\text{CaSO}_4$ . Thus, both the relations (1) and (2) are applicable.

Dividing equation (1) by equation (2), we get

$$\frac{K_{\text{CaCO}_3}^{\text{sp}}}{K_{\text{CaSO}_4}^{\text{sp}}} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}$$

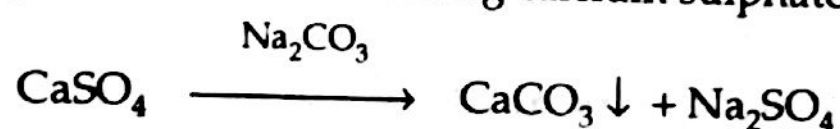
$$\Rightarrow K' = \frac{[\text{CO}_3^{2-}]}{[\text{SO}_4^{2-}]} \quad \dots(3)$$

if  $K' < \frac{[\text{CO}_3^{2-}]}{[\text{SO}_4^{2-}]}$

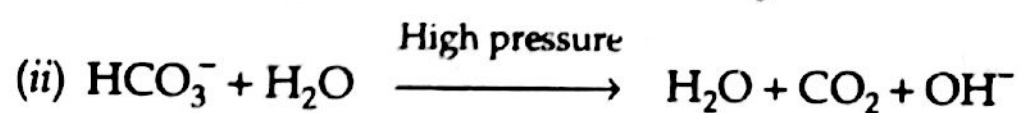
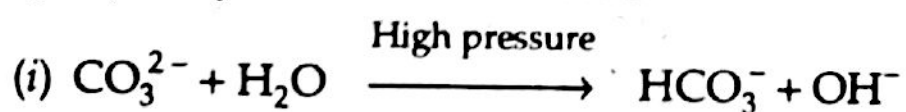
or if  $[\text{CO}_3^{2-}] > K' [\text{SO}_4^{2-}]$

then only  $\text{CaCO}_3$  will be precipitated in preference to  $\text{CaSO}_4$ . This is because the solubility product of  $\text{CaSO}_4$  cannot be attained under these conditions.

These principles are used in the **carbonate conditioning**. When sodium carbonate solution is added to boiler water, the  $[\text{CO}_3^{2-}]$  increases and when it becomes greater than  $K' [\text{SO}_4^{2-}]$ , only  $\text{CaCO}_3$  gets precipitated. Moreover,  $\text{CaSO}_4$  remains in solution so the deposition of scale-forming calcium sulphate is prevented.



In high-pressure boilers, scale formation cannot be avoided by adding sodium carbonate to boiler water. This is because, in high pressure boiler, the  $\text{CO}_3^{2-}$  ions undergo hydrolysis to form  $\text{OH}^-$  ions.



Because of the above two hydrolysis reactions (i) and (ii), the concentration of carbonate ions (i.e.,  $[\text{CO}_3^{2-}]$ ) gets reduced. Thus, it becomes impossible for solution to become saturated w.r.t. calcium or magnesium carbonate. As a consequence, precipitation and subsequent loose sludge formation due to  $\text{CaCO}_3$  or  $\text{MgCO}_3$  becomes impossible.

Moreover, due to hydrolysis reactions (i) and (ii), the hydroxide ion concentration (i.e.,  $[\text{OH}^-]$ ) becomes high which can lead to caustic embrittlement.

**To sum up :** Carbonate conditioning is not done in high pressure boilers, because (a) it is not applicable, (b) It may lead to caustic embrittlement.

### Solved Example on Carbonate Conditioning

**Example 1.** In an experiment to determine the hardness of a sample of water, 25 mL of N/50  $\text{Na}_2\text{CO}_3$  solution was added to 100 mL of water sample. After completion of precipitation of insoluble carbonate, the unreacted  $\text{Na}_2\text{CO}_3$  was titrated against N/50  $\text{H}_2\text{SO}_4$  solution, when 10 mL of the acid was required. Calculate the hardness and comment on the nature of hardness so determined.



**Solution.** Given, Normality of  $\text{Na}_2\text{CO}_3 = N_1 = N/50$

Effective volume of  $\text{Na}_2\text{CO}_3$  used  $= V_1 = 25 - 10 = 15 \text{ mL}$

Volume of hard water  $= V_2 = 100 \text{ mL}$

Let Normality of hard water  $= N_2$

Applying the Normality equation,

$$N_1 V_1 = N_2 V_2$$

$$\Rightarrow \frac{N}{50} \times 15 = N_2 \times 100$$

$$\Rightarrow N_2 = \frac{15}{50} \times \frac{1}{100} N$$

$$\text{Now, Strength} = N_2 \times 50 \text{ g/L}$$

$$= \frac{15}{50} \times \frac{1}{100} \times 50 = 0.15 \text{ g/L}$$

$$= 0.15 \times 1000 \text{ mg/L} = 150 \text{ mg/L}$$

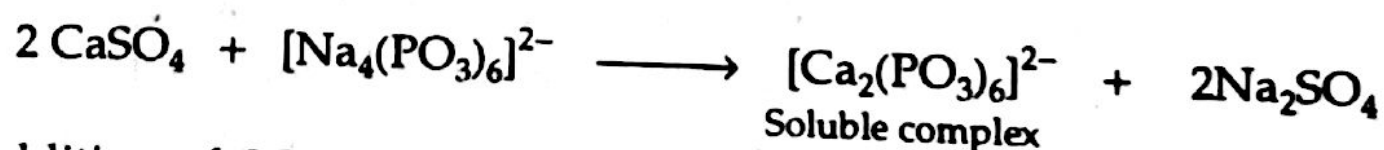
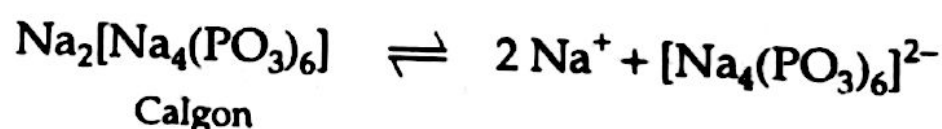
$$\Rightarrow \text{Hardness} = 150 \text{ ppm}$$

We know that in carbonate conditioning, sodium carbonate removes permanent hardness causing ions.

Thus, Permanent hardness of water  $= 150 \text{ ppm}$ .

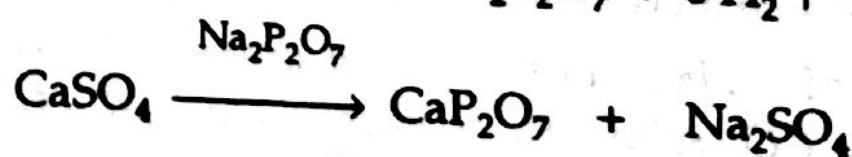
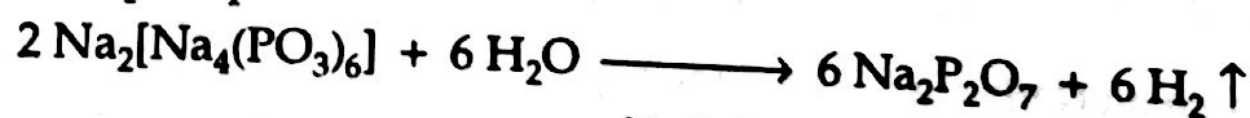
### 12.3 Calgon Conditioning

It involves in adding sodium hexa meta phosphate (also known as calgon) to boiler water to prevent the scale and sludge formation. Calgon converts the scale forming impurity like  $\text{CaSO}_4$  into soluble complex compound, which are harmless to boiler.



Addition of 0.5 – 5 ppm of calgon prevents scale formation in one of the following ways:

- (i) At low temperatures and pressures, it forms quite stable and soluble complexes with calcium salts,
- (ii) At high temperatures and pressures, calgon is converted into sodium orthophosphate which reacts with calcium salts to form calcium orthophosphate.



Calcium orthophosphate  
(loose sludge)

Calcium orthophosphate appears as loose sludge and thus can be removed by blow-down operation.

### Limitations of Calgon Conditioning

Calgon conditioning is not applicable for the prevention of iron oxide and copper depositions.

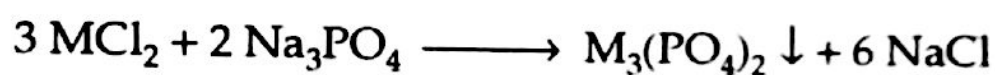
However, iron oxide and copper depositions can be prevented by adding EDTA or its sodium salt to the boiler water. In this method, the problem causing cations are converted into complexes, which will stay in "dissolved form" in water and thus do not cause any harm.

This is because, the solubility product of  $\text{CaSO}_4$  cannot be exceeded under these conditions and hence  $\text{CaSO}_4$  scale will not form.

These principles are used in phosphate conditioning, in which an excess of a properly chosen phosphate is added to the boiler water. This will help in the precipitation of the residual  $\text{Ca}^{2+}$  ions in the form of non-adherent precipitate of calcium phosphate and thus the scale formation is prevented.

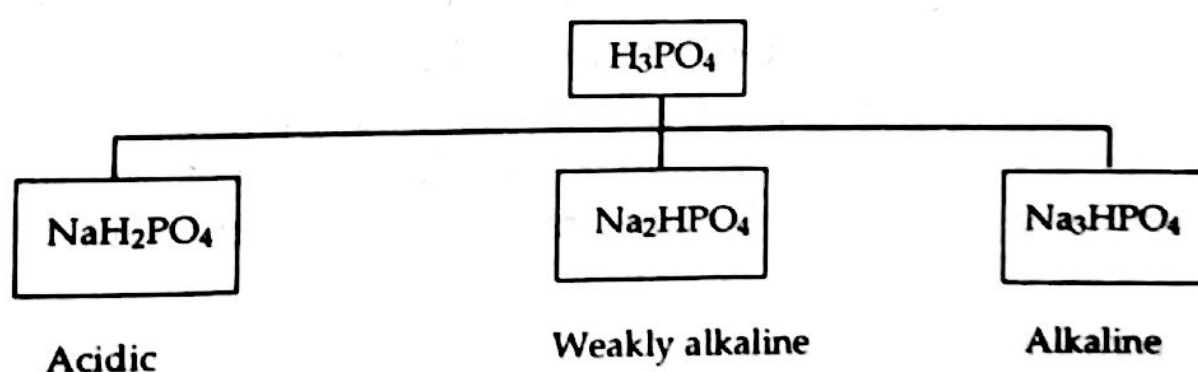
### 12.4 Phosphate Conditioning

It is applicable to high-pressure boilers. Scale formation is avoided by adding sodium phosphate, which reacts with magnesium and calcium salts forming non-adherent and easily removable, soft sludge of calcium and magnesium phosphate, the later can be removed by blow-down operation, e.g.,



where  $\text{M} = \text{Ca}^{2+}$  or  $\text{Mg}^{2+}$

The choice of phosphate salt depends upon the alkalinity of the boiler-feed water. Calcium can be precipitated properly at a pH of 9.5 or above so a phosphate is selected that adjusts pH to optimum value (9.5-10.5).

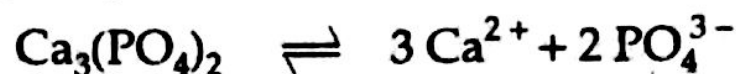


Trisodium phosphate  $\text{Na}_3\text{PO}_4$  (alkaline) is most suitable for treatment, when the alkalinity of boiler water is low as it is most alkaline in nature. If the alkalinity of boiler water is sufficient, then disodium phosphate [ $\text{Na}_2\text{HPO}_4$  (weakly alkaline)] is selected. But if the alkalinity of boiler water is too high and requires to be reduced, then sodium dihydrogen phosphate [ $\text{NaH}_2\text{PO}_4$  (acidic)] is used.

Consider a solution saturated with both  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaSO}_4$ . In this situation, the solubility product equations for both calcium phosphate and calcium sulphate salts must be satisfied.



For calcium phosphate



∴ Solubility product of calcium phosphate

$$\left( K_{\text{Ca}_3(\text{PO}_4)_2}^{\text{sp}} \right) = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 \quad \dots(1)$$

$$\Rightarrow \left( K_{\text{Ca}_3(\text{PO}_4)_2}^{\text{sp}} \right)^{1/3} = [\text{Ca}^{2+}] [\text{PO}_4^{3-}]^{2/3} \quad \dots(2)$$

Similarly, for calcium sulphate



∴ Solubility product of calcium sulphate

$$\left( K_{\text{CaSO}_4}^{\text{sp}} \right) = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \quad \dots(3)$$

Dividing equation (2) by equation (3), we have

$$\frac{\left( K_{\text{Ca}_3(\text{PO}_4)_2}^{\text{sp}} \right)^{1/3}}{\left( K_{\text{CaSO}_4}^{\text{sp}} \right)} = \frac{[\text{PO}_4^{3-}]^{2/3}}{[\text{SO}_4^{2-}]} = K'' \quad (\text{let})$$

$$\Rightarrow [\text{PO}_4^{3-}]^{2/3} = K'' [\text{SO}_4^{2-}] \quad \dots(4)$$

Moreover, as long as

$$[\text{PO}_4^{3-}]^{2/3} > K'' [\text{SO}_4^{2-}],$$

only  $\text{Ca}_3(\text{PO}_4)_2$  will be precipitated in preference to  $\text{CaSO}_4$ .

### 13 DOMESTIC WATER TREATMENT

#### *Access to good quality drinking water*

Access to good quality drinking water is essential to human health. The World Health Organisation estimates that nearly a quarter of the world's six billion people currently lack access to good quality water for drinking, personal hygiene, domestic use or sanitation. As the global population increases, and scientists predict that changes in the global environment will make our lives more drier, the access to good quality drinking water will become major global challenge for the new century.

#### *Standards for drinking water*

The standards for drinking water can be broadly classified into following two types :

(i) **Primary standards.** These standards specify the maximum contaminant levels (MCL) of various contaminants based on their effect on human health. If the concentration of these contaminants is greater than permissible MCL, then serious health effects will occur.

For instance, the MCL for lead is 0.050 mg/L. If it is exceeded then it causes liver and kidney damages, mental retardation in children, abnormalities in fertility and pregnancy and gastro-intestinal damages.

(ii) **Secondary standards.** Depending upon the hardness, colour, odour and taste, these 2° standards vary from place to place and they do not have any anticipated ill effects on health.

*Drinking or potable* water is fit for human consumption. The common specifications or standards prescribed and recommended for drinking water are as follows :

- (i) It should be colourless and odourless,
- (ii) It should be good in taste,
- (iii) It should not be hot,
- (iv) Its turbidity should be less than 10 ppm,
- (v) It should be free from objectionable dissolved gases like  $H_2S$ ,
- (vi) It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts,
- (vii) Its alkalinity should not be high. pH should be in the range of 7.0 – 8.5.
- (viii) It should be reasonably soft, total hardness should be less than 500 ppm.
- (ix) It should be free from disease-producing microorganisms.
- (x) chloride, Fluoride and sulphate contents should be less than 250 ppm, 1.5 ppm and 250 ppm respectively.

The following table summarises water quality standards :

**Table 12 : Standards for drinking water**

S.No.	Parameter	Standard	
		ISI (mg/L)	WHO (mg/L)
1.	Colour, Odour and Taste	Colourless, Odourless and Tasteless	Colourless, Odourless and Tasteless
2.	pH	6.9	6.9
3.	Total dissolved solids	—	1,500
4.	Dissolved oxygen	3.0	—
5.	Chloride	600	250
6.	Sulphate	1,000	400
7.	Nitrate	—	45
8.	Cyannide	0.01	0.2
9.	Fluoride	3.0	1.5
10.	Chromium	0.05	0.05
11.	Lead	0.1	0.05
12.	Arsenic	0.2	0.05

☞ When water from the source (like river or lake) is stored in a reservoir for its treatment for domestic use, what is the purpose of (i) pumping a dispersion of powdered long chain aliphatic alcohols (like *n*-hexadecanol) through orificed lines along the edges of the reservoir, and (ii)  $CuSO_4$  addition.

**Ans.** (i) To minimize any loss of water due to evaporation. (ii) To prevent the growth of algae which may impart an unpleasant taste to water.



### Treatment of Water for Domestic Purposes

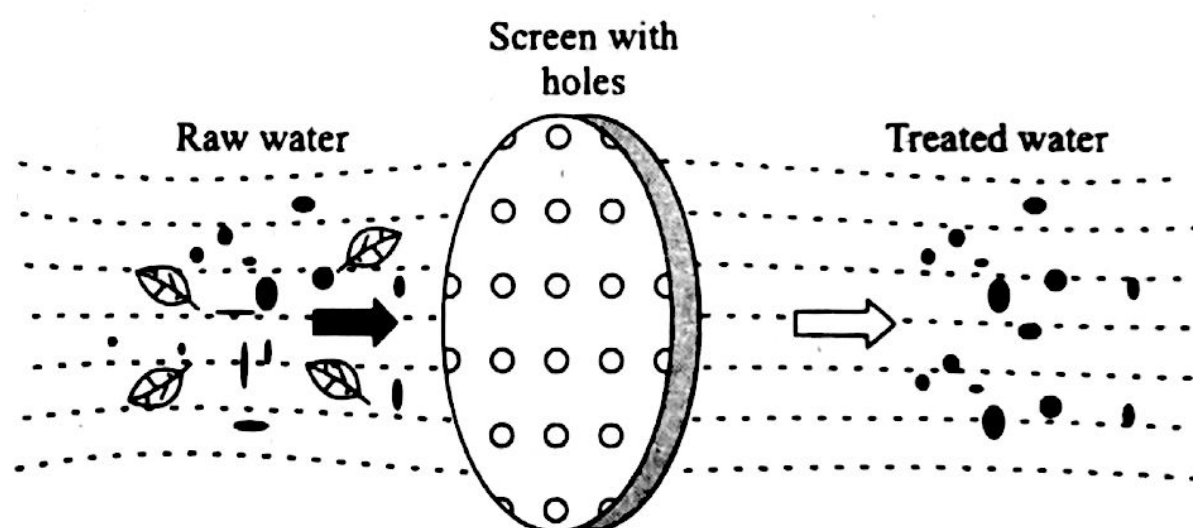
Municipalities have to supply potable water. Rivers, lakes and wells are the most common sources of water used by them. Natural water from these sources do not confirm to all the required specifications of drinking water. Hence to make these waters – potable, treatment has to be given. Actual treatment methods adopted, depend upon the exact nature of impurities present in raw water. Table 13 lists the types of impurities and the processes to be employed for removing them.

**Table 13 : Treatment processes for drinking water**

S.No.	Impurity	Process used for removal
1.	Floating matter such as leaves, wood pieces, etc.	Screening
2.	Suspended impurity such as sand, clay etc.	Sedimentation
3.	Fine suspended inorganic matter	Sedimentation with coagulation
4.	Microorganisms and colloidal impurities	Filtration
5.	Pathogenic bacteria	Disinfection

These methods are briefly discussed below :

(i) **Screening.** It is a process of removing floating materials like wood pieces, leaves, etc. from water. Raw water is passed through screens having holes, when the floating matter is retained by them and water is allowed to pass.



**Fig. 22.** Screening for removal of floating matter.

(ii) **Sedimentation.** The process of subsidence and deposition of suspended matter from a waste water by gravity is termed as sedimentation.

In other words, the sinking of a molecule under the opposing forces of gravitation and buoyancy is sedimentation. Furthermore, **sediment** is any particulate matter that can be transported by fluid flow and which eventually is deposited as a layer of solid particles on the bed or bottom of a body of water or other liquid.

It is the process of removing suspended impurities by allowing the water to stand undisturbed in big tanks for 2 – 8 hours. Most of the particles settle down at the bottom of the tank due to gravitational force, and they are removed. The clear supernatant water is then drawn out from the tank. This process removes only 70-75% of the suspended matter.

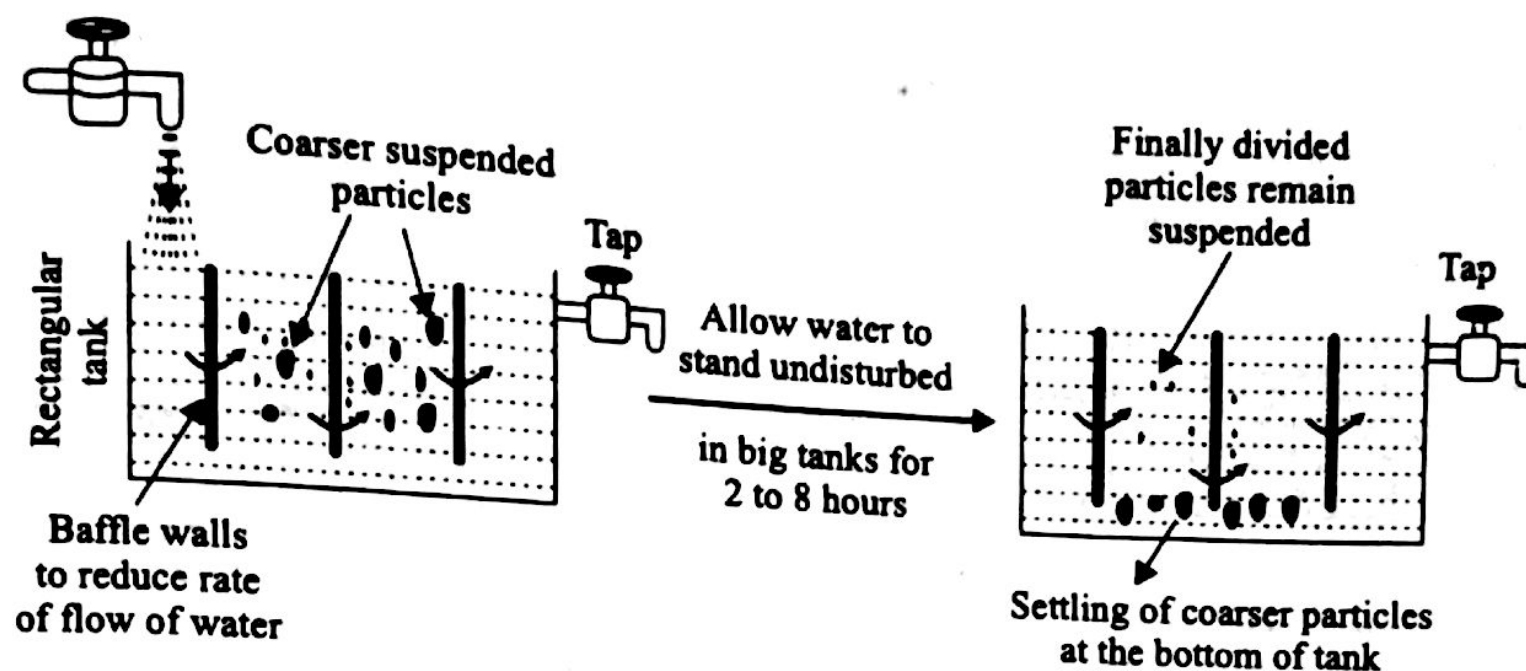


Fig. 23. Sedimentation for removal of coarser suspended impurities.

(iii) *Sedimentation with coagulation.* Finely divided silica, clay and organic matter do not settle down easily and hence cannot be removed by mere sedimentation. Most of these are in colloidal form and carry negative charge. Thus, they do not coalesce due to mutual repulsions. For their removal coagulation is required. In this process, coagulants like Alum [ $K_2(SO_4)_3 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ] or sodium aluminate ( $NaAlO_2$ ) is added to water which hydrolyses to form a gelatinous precipitate of  $Al(OH)_3$ . This insoluble, flocculant precipitate descent through the water, absorbs and entangles very fine suspended impurities forming bigger flocs, which settle down easily. Moreover, coagulants like alum provide  $Al^{3+}$  ions which neutralize the negatively charged colloidal particles when they come closer and combine to form bigger particles. Due to the force of gravity, these bigger particles settle down.

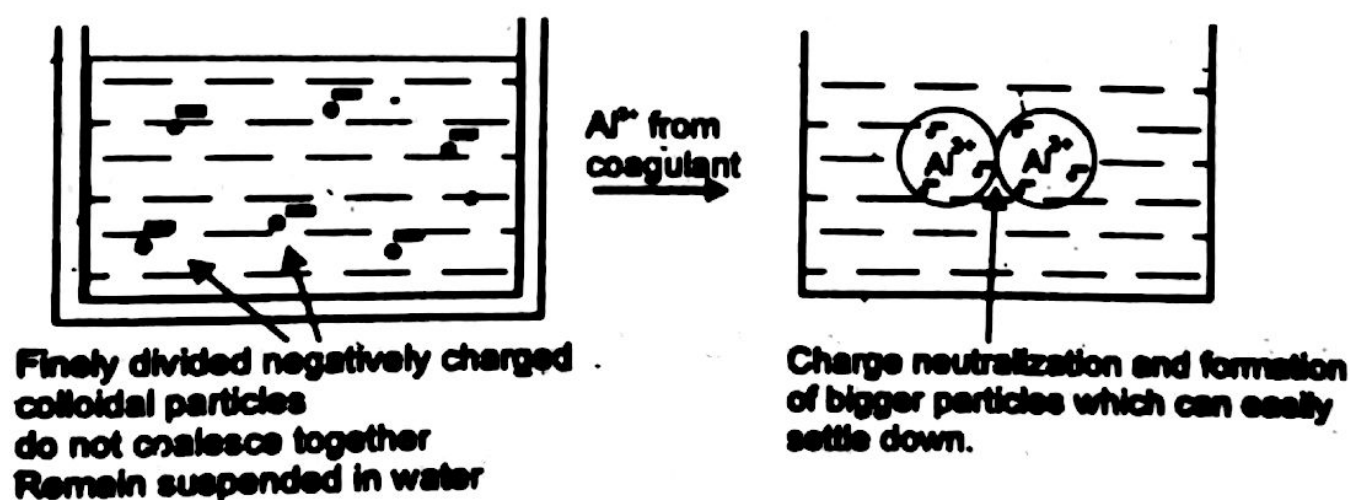
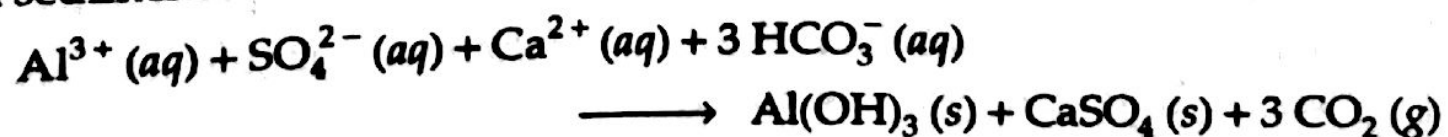


Fig. 24. Illustration of action of coagulants.

Coagulant like aluminium sulfate (alum,  $Al_2(SO_4)_3$ ) react with ions naturally found in the water to produce a solid precipitate (equation 1). As this precipitate forms, other particles are caught in the solid, forming a mass that will settle to the bottom via sedimentation.





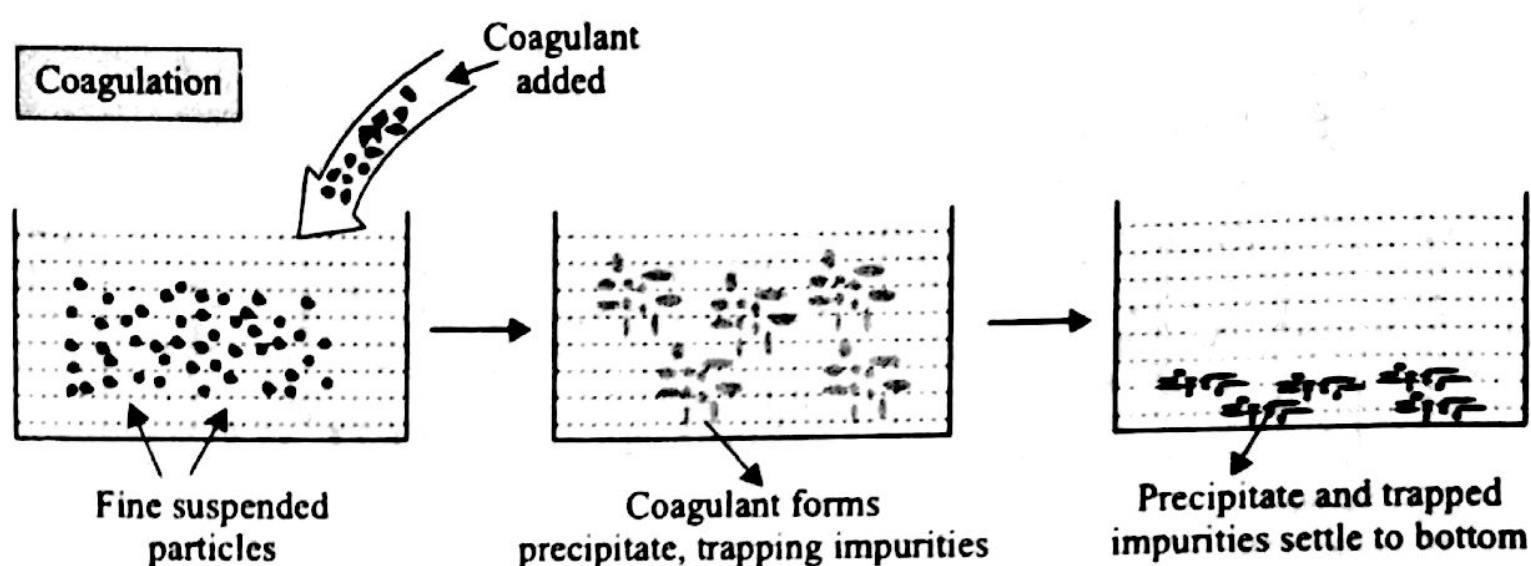


Fig. 25. Illustration of coagulation.

The most commonly used coagulants and their ideal pH range of use are summarized below :

	Chemical coagulants	Ideal pH range of use	*1
(a)	$\text{Al}_2(\text{SO}_4)_3$ (Alum)	6.5 – 8.5	*2
(b)	$\text{NaAlO}_2$ (sodium aluminate)	5.5 – 8.0	*3
(c)	$\text{FeSO}_4$ (Ferrous sulphate)	> 8.5	*4

\*1  $\equiv$  Involved chemical reactions

\*2  $\equiv \text{Al}_2(\text{SO}_4)_3 + 3 \text{Ca}(\text{HCO}_3)_2 \longrightarrow 2 \text{Al}(\text{OH})_3 \downarrow + 3 \text{CaSO}_4 + 6 \text{CO}_2$

\*3  $\equiv \text{NaAlO}_2 + 2 \text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 \downarrow + \text{NaOH}$

\*4  $\equiv \text{FeSO}_4 + \text{Mg}(\text{HCO}_3)_2 \longrightarrow \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O} + \left\{ \text{Fe}(\text{OH})_2 \xrightarrow{(\text{O}_2 + \text{H}_2\text{O})} \text{Fe}(\text{OH})_3 \right\}$

☞ What is coagulation ?

Ans. Coagulation refers to the process of agglomeration of colloidal particles by adding certain chemicals such as  $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$ ,  $\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  etc.

☞ Explain, in brief, the coagulating action of polymeric electrolytes (called polyelectrolytes).

Ans. This can be explained by 'inter-particle bridging theory'. As per this, the functional groups in the polymer get adsorbed at the surface of a colloidal particle, the rest of the molecule extending out into the solution. A particle-polymer-particle complex is formed when a second particle with some vacant adsorption sites comes into contact with the extended segments. Such complex formation helps in coagulation.

**Sludge** is defined as "the accumulated solids or precipitate removed from a sedimentation basin, settling tank, or clarifier in a water treatment plant. The accumulated solids are the result of chemical coagulation, flocculation, and sedimentation of raw water.

(iv) **Filtration.** For further purification of water and for removing micro-organisms, odour, colour taste and fine-suspended particles, filtration is done. **Water filtration** is the process of separating particles of various nature and size from water or waste water by passage through a porous medium which is generally a bed of sand or similar particles. Water flows through the pores between the filter grains and the impurities are left behind, either clogged in the open spaces or attached to the filter medium itself. The particles removed in direct filtration range in size from 0.1 to 100 mm. The main uses of water filters are to remove colour, turbidity, taste, odours and microorganisms.

There are different types of filters like gravity filter, slow sand filter, rapid sand filter and pressure filters ; the rate of flow of water also increasing in that orders.

### Gravity Filtration

Water containing solid impurities enters the filter through an inlet at the top and is forced by gravity through layers of sand and gravel. The solids gets trapped between the sand and gravel pieces. The water that emerges into the under drain at the bottom of the filter is cleaned of these solids and exits the filter through an outlet at the bottom.

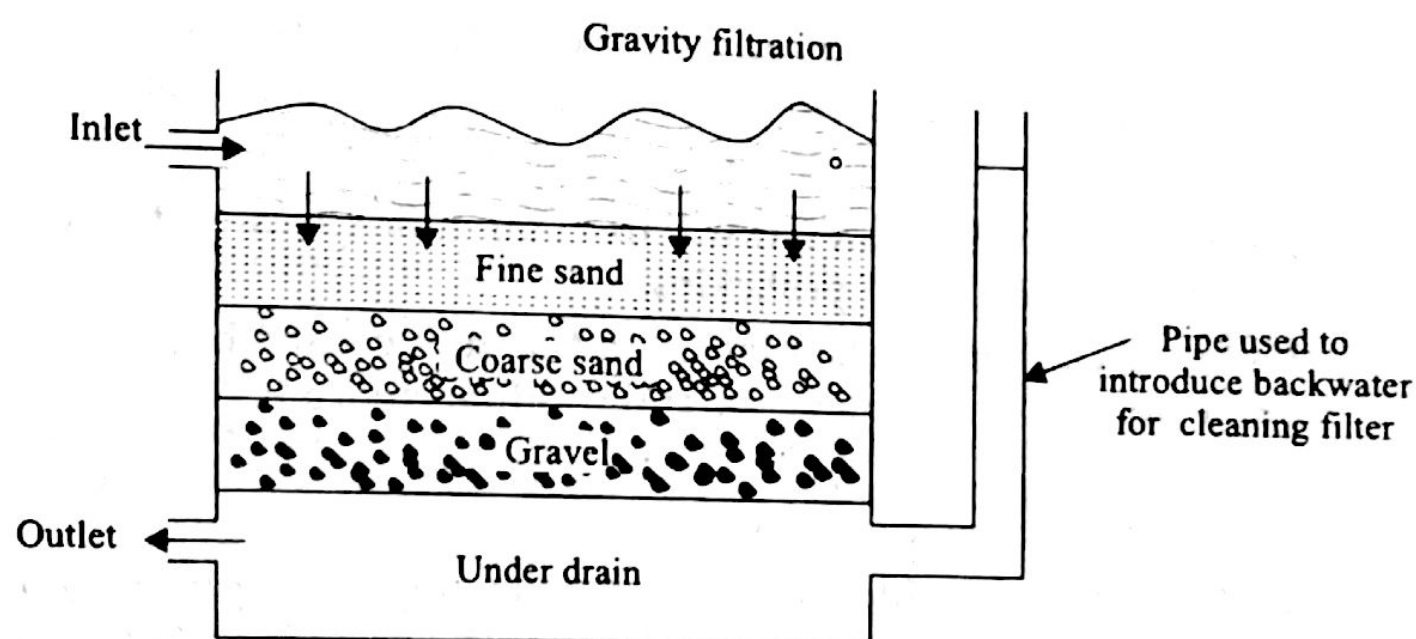


Fig. 26. Gravity filtration.

Gravity filters have a pipe feeding into the under drain, the bottom layer where the clean water is collected. By adding water to the filter through this pipe, clean water can be forced upward through the filter to remove the solids that have collected in the filter. This process is used to clean the filter.

### Operation of sand filter

A typical sand filter consists of a tank containing beds of fine sand (top layer), coarse sand, fine gravel and coarse gravel (bottom layer). The tank is provided with inlet for sedimented water and an underdrain channel at the bottom for exit of filtered water. Sedimented water entering the sand filter is distributed uniformly over the entire fine sand bed and it flows through the various beds slowly due to gravity. Due to retention of impurities in the pores, the sand pores get eventually clogged and the rate of filtration slowly decreases. When it becomes very slow, filtration is stopped and the bed is cleaned by scraping of a small layer of the sand bed (top layer) and replacing it with clean sand. The scrapped sand is washed with water, dried and stored for reuse at the time of next scrapping operation.



**Activated carbon filtration system** involves the adsorption (adhesion) of one material on the surface of a second solid substance based on opposing electrical charges of each material.

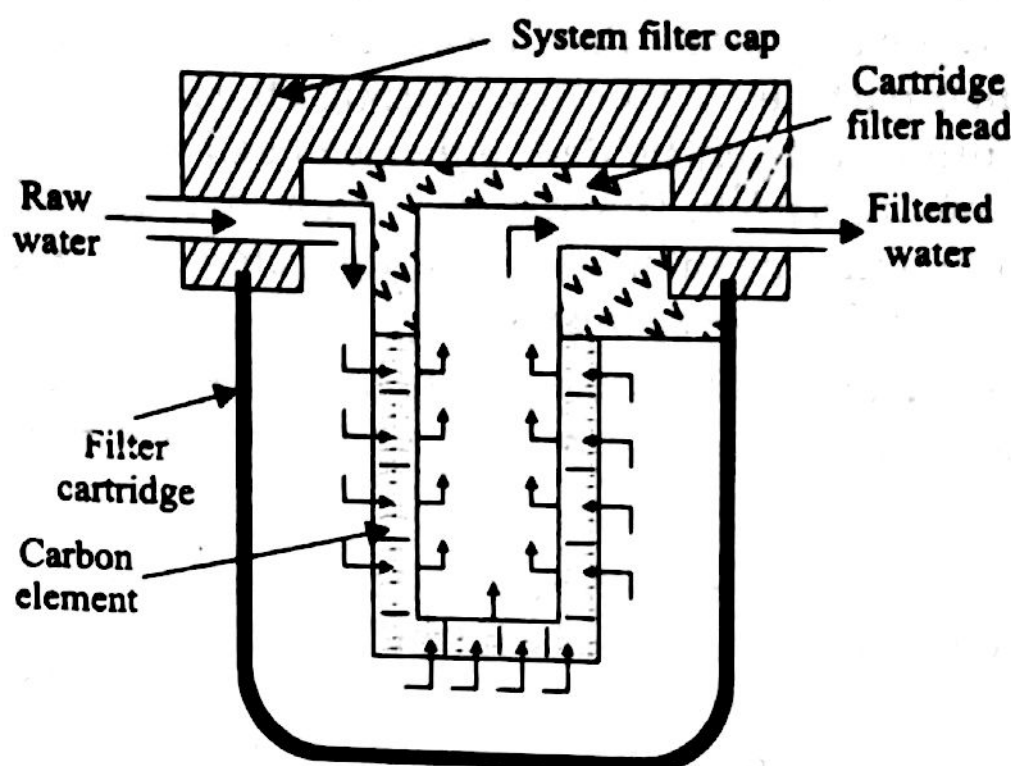


Fig. 27. Cartridge type activated carbon or charcoal filter.

Activated carbon is placed on a filter medium or installed in treatment tanks and adsorbs the taste and odour impurities in water, leaving the water taste and odour free.

**Uses :**

- (i) For eliminating certain hazardous compounds related to industrial wastes, chemicals and pesticides.
- (ii) For removing unpleasant tastes and odours caused by decaying organic matter, dissolved gases, and residual chlorine.

**Limitations :**

- (i) Does not treat microorganisms.
- (ii) Water has to be chlorinated before passing through an activated carbon filter so as to prevent bacteriological growth on the filter.

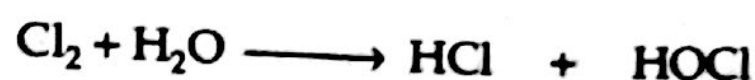
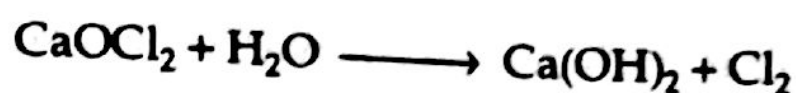
(v) **Removal of micro-organisms.** Even after filtration, water still contains a small percentage of disease producing (pathogenic) bacteria which must be removed or destroyed if the water has to be used for drinking or municipal purposes. The process of destroying/killing the pathogenic bacteria, micro-organisms etc. from the water to make it safe for use is known as *disinfection*. It does not ensure total destruction of all living organisms. On the other hand, *sterilisation* means complete destruction of all living organisms. It is done by boiling the water for a period of time. sterilisation is a costly process and is used only by individuals particularly during the break up of epidemics in the town or city. It can not be employed in municipal water-works as it kills the bacteria only at the time of boiling but does not provide any protection against future contamination.

**Characteristics of an ideal disinfectant**

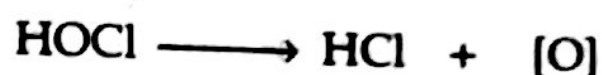
- (i) It should kill the disease producing micro-organisms quickly at room temperature, (ii) It should be inexpensive, (iii) It should not be toxic to human, and (iv) It should provide protection against any contamination in water during conveyance or storage.

**Method of disinfection of water**

(A) *By adding bleaching powder.* The chemical reaction of bleaching powder in water is given below :



Hypochlorous acid



Nascent oxygen

It was earlier believed that nascent oxygen (thus liberated) destroys the pathogens by oxidation. In fact, enzymes in the cells of organisms get deactivated by their chemical reaction with hypochlorous acid. As enzymes are essential for the metabolic process of the micro-organisms so their inactivation results in the death of micro-organisms.

*Drawbacks of using bleaching powder :* (a) Excess of bleaching powder imparts bad taste and smell to treated water. Thus only calculated quantity of it should be used. (b) It is not stable so it deteriorates due to its continuous decomposition during storage. (c) It introduces calcium in water and thus increases hardness.

(B) *By Chlorination.* Chlorine is the most commonly used disinfectant in water treatment. It can be employed directly as a gas or in the form of concentrated solution in water. It produces hypochlorous acid, which is a powerful germicide. Apparatus used for disinfection by chlorine is known as chlorinator (see Fig. 28). It is a large tower which contains number of baffle plates. From its top, raw water and chlorine solution are introduced. These get thoroughly mixed during their passage through the tower. For filtered water, about 0.3 – 0.5 ppm of  $\text{Cl}_2$  is sufficient. Disinfected water is taken out from the outlet at the bottom of chlorinator.

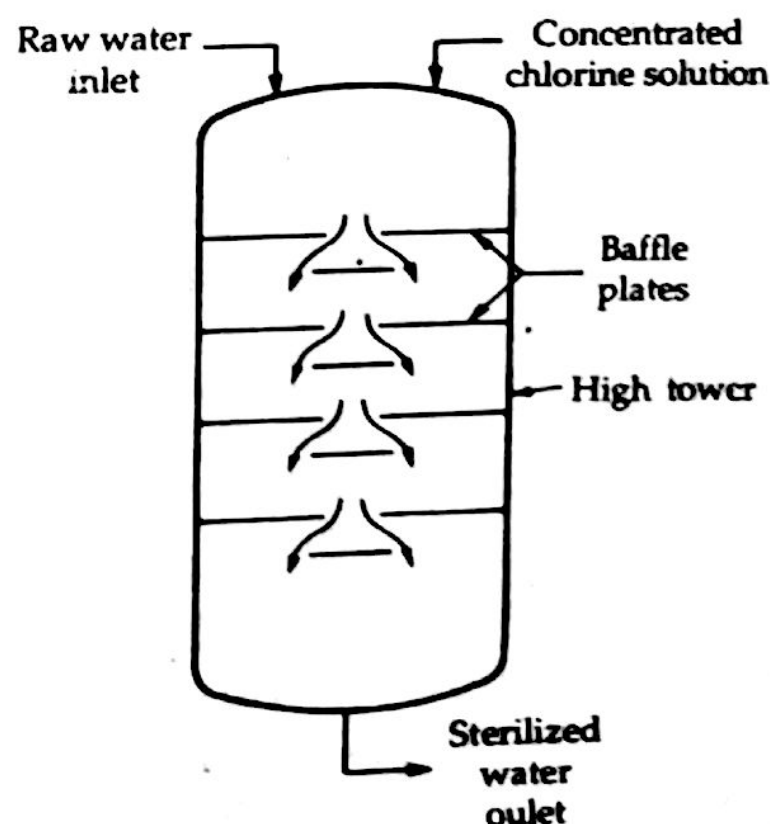


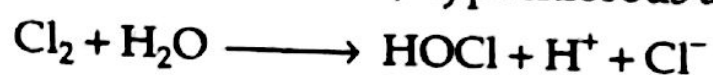
Fig. 28. Chlorinator.



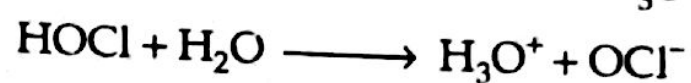
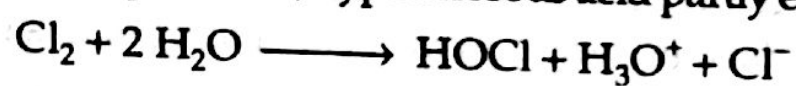
### Mechanism of Chlorine Disinfection

Chlorine kills pathogens such as bacteria and viruses by breaking the chemical bonds in their molecules. Disinfectants that are used for this purpose consist of chlorine compounds which can exchange atoms with other compounds, such as enzymes in bacteria and other cells. When enzymes come in contact with chlorine, one or more of the hydrogen atoms in the molecule are replaced by chlorine. This causes the entire molecule to change shape or fall apart. When enzymes do not function properly, a cell or bacterium will die.

When chlorine is added to water, hypochlorous acid is formed :



Depending on the pH value, hypochlorous acid partly expires to hypochlorite ions :



Hypochlorite ions fall apart to chlorine and oxygen atoms :



The disinfecting properties of chlorine in water are based on the oxidising power of the free oxygen atoms and on chlorine substitution reactions.

Hypochlorous acid (HOCl, which is electrically neutral) and hypochlorite ions ( $\text{OCl}^-$ , electrically negative) will form free chlorine when bound together. This results in disinfection.

HOCl is more reactive and is a stronger disinfectant than  $\text{OCl}^-$ . HOCl is split into HCl and atomic oxygen (O). The oxygen atom is a powerful disinfectant.

By nature, the cell wall of pathogenic microorganisms is negatively charged. As such, it can be penetrated by the neutral HOCl, rather than by the negatively charged  $\text{OCl}^-$ . HOCl can penetrate cell walls, slime layers and protective layers of microorganisms and effectively kills pathogens as a result. The microorganisms will either die or suffer from reproductive failure.

The effectivity of disinfection is determined by the pH of the water. Disinfection with chlorine will take place optimally when the pH is between 5.5 and 7.5. Hypochlorous acid reacts faster and is 80 – 100% more effective than  $\text{OCl}^-$ .

The level of HOCl will decrease when the pH value is higher.

S.No.	pH	[HOCl]	[OCl <sup>-</sup> ]
1.	6	80%	20%
2.	7.5	50%	50%
3.	8	20%	80%

### Free and Bound Chlorine

For disinfection purposes, when  $\text{Cl}_2$  is added to water, it usually starts reacting with dissolved organic and inorganic compounds in the water. Chlorine can no longer be used for disinfection after that, because it has formed other products. The amount of chlorine that is used during this process is referred to as the 'chlorine enquiry' of the water.

Chlorine can react with ammonia ( $\text{NH}_3$ ) to form chloramines. These compounds are referred to as 'active chlorine compounds', contrary to  $\text{HOCl}$  and  $\text{OCl}^-$ , which are referred to as 'free active chlorine' and are responsible for water disinfection. However, these compounds react much more slowly than free active chlorine.

#### *Factor affecting efficiency of chlorine*

(i) *Temperature of water.* Death rate of micro-organisms (*i.e.*, number of micro-organisms destroyed per unit time) is directly proportional to temperature. Thus, efficiency increases with rise in temperature.

(ii) *Time of contact.* Death rate of micro-organisms by chlorine is proportional to the number of micro-organisms remaining alive. Initially, the death rate is maximum and with time, it goes on decreasing.

(iii) *pH of water.* To kill same % of organisms, a small contact period is required at lower pH values (between 5-6.5).

#### *Advantages of using chlorine as disinfectant*

(i) The use of chlorine is more effective and economical,

(ii) It is stable, requires small space for storage and does not deteriorate on keeping,

(iii) It can be used at high as well as low temperatures,

(iv) It does not introduce any impurity in treated water

To sum up, chlorine is the most ideal disinfectant.

#### *Disadvantages of using chlorine as disinfectant*

(i) If excess of chlorine is added, it produces bad taste and disagreeable odour.

(As a result of chlorination of phenols, leading to the formation of chlorophenols, water acquires a peculiar odour.)

(ii) Excess chlorine produces irritation on mucous membrane,

(iii) It is not effective at higher pH values.

"The treated water should not contain more than 0.1-0.2 ppm of free chlorine".

#### *Break-point chlorination*

It means the chlorination of water to such an extent that living organism as well as other organic impurities in water are destroyed. It involves in addition of sufficient amount of chlorine to oxidise organic matter, reducing substances, and free ammonia in raw water, leaving behind mainly free chlorine which possesses disinfecting action against pathogenic bacterias. It is also known as *free-residual chlorination*. A typical relationship between the amount of chlorine added to water and the experimentally determined free residual chlorine is shown in Fig. 29.

**Stage I:** Initially for lower doses of  $\text{Cl}_2$ , there is no free residual chlorine since all the added chlorine gets consumed for doing complete oxidation of reducing substances present in water.

**Stage II:** As the amount of chlorine dosage is increased, amount of residual chlorine (experimentally determined) also show steady increase. This stage corresponds to the formation of chloro-organic compounds without oxidising them.



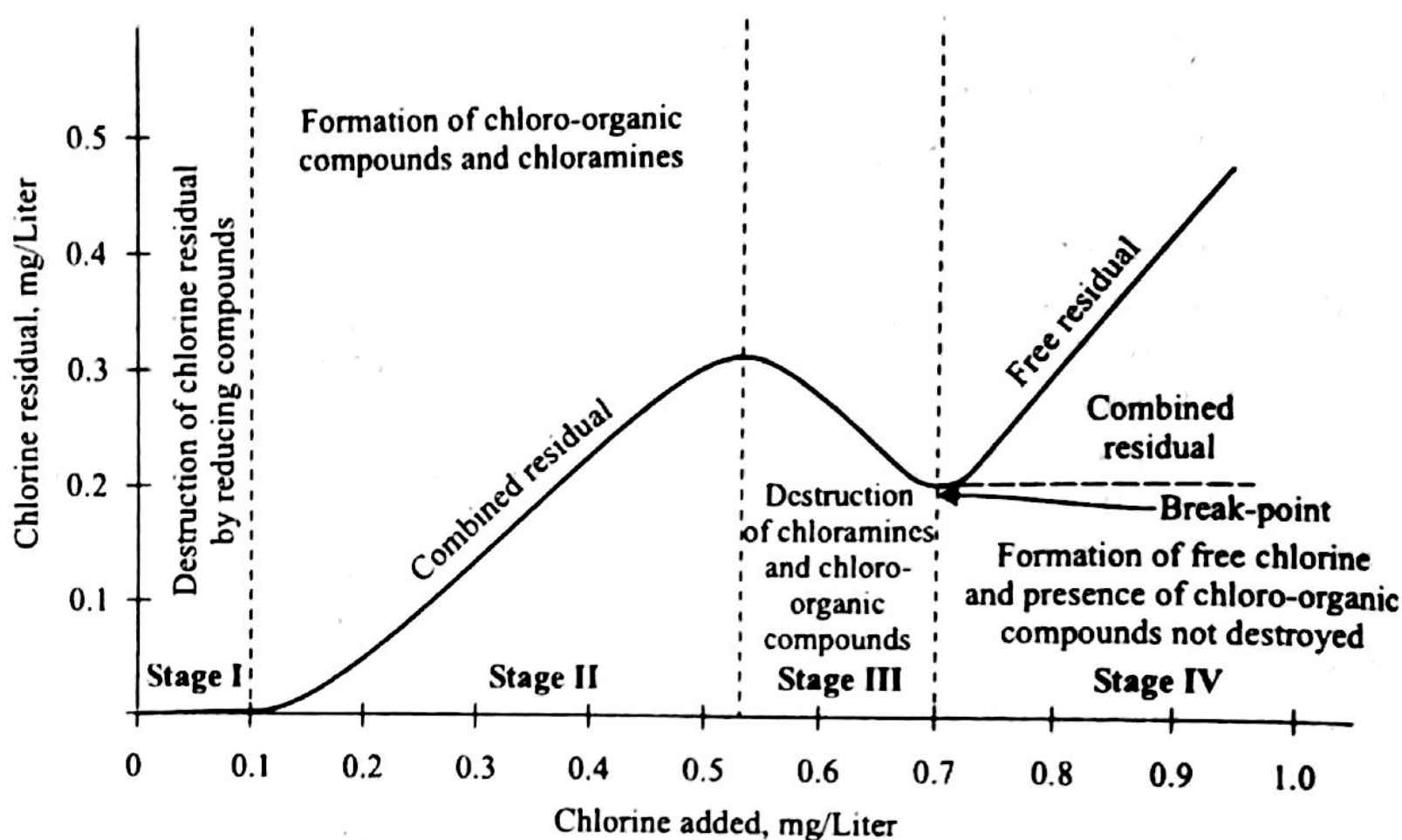


Fig. 29. Break-point chlorination curve.

**Stage III:** At still higher dose of applied chlorine, oxidation of organic compounds and micro-organisms sets in consequently the amount of free residual chlorine also decreases. When the oxidative destruction is complete it reaches a minima.

**Stage IV:** After minima, the added chlorine is not used in any reaction. Thus, the residual chlorine keeps increasing in direct proportion to added chlorine.

Hence, for effectively killing the micro-organisms, sufficient chlorine (corresponding to minima in the curve) has to be added. Addition of chlorine in such dosages is known as break-point or free residual chlorination.

#### *Advantages of break-point chlorination*

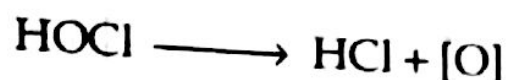
- (i) It ensures complete destruction of organic compounds which impart colour, bad odour and unpleasant taste to water ;
- (ii) It completely destroys all the disease producing bacteria ; and
- (iii) It prevents the growth of any weeds in water.

#### *De-chlorination*

Over chlorinated water can be de-chlorinated by passing it through bed of molecular carbon or by adding activated carbon to water and removing it by filtration after the reaction period. The excess chlorine can also be removed by the addition of small quantities of reducing substances like sulphur dioxide ( $\text{SO}_2$ ),  $\text{Na}_2\text{SO}_3$ , etc.



(C) *By using Chloramine ( $\text{ClNH}_2$ )*. Chloramine has better bactericidal action than chlorine



as it is more stable and does not produce any irritating odour. It is obtained by mixing chlorine and ammonia in 2:1 ratio.

(D) *Disinfection by Ozone ( $\text{O}_3$ )*. Ozone is made by passing silent electric discharge through cold and dry oxygen and is highly unstable, as it liberates nascent oxygen after breakdown  $\text{O}_3 \rightarrow \text{O}_2 + [\text{O}]$

In fact ozone is an excellent and harmless disinfectant since it produces nascent oxygen which is a powerful oxidising agent. It oxidises the organic matter present in water and also kills the bacteria. Disinfection of water by ozone is carried out in ozone sterilizer, shown in Fig. 30.

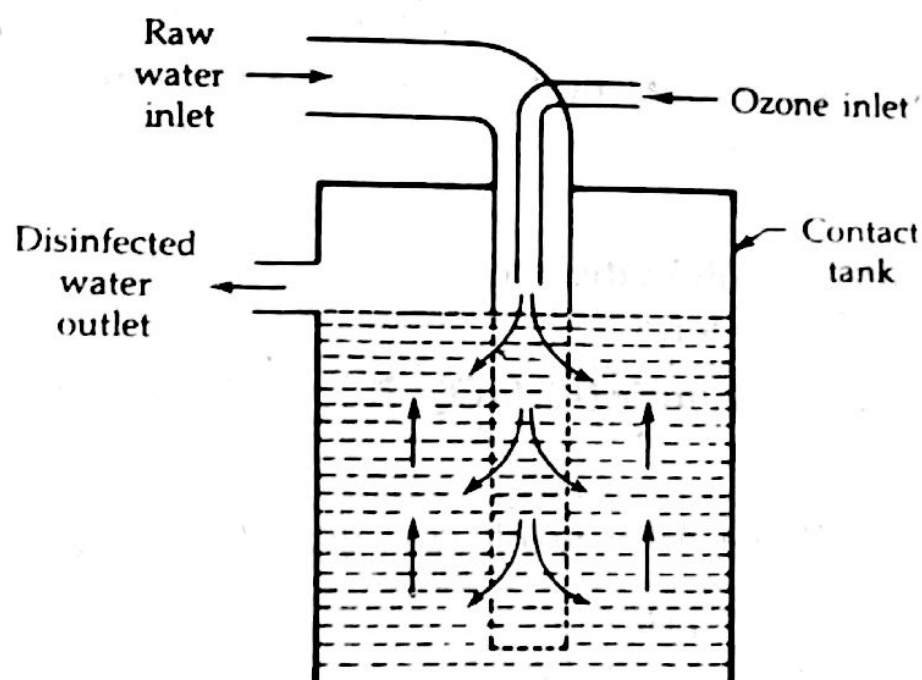


Fig. 30. Ozone sterilizer.

Ozone (2-3 ppm) is injected into the water and the two are allowed to come in contact in a sterilizing tank for about 10-15 minutes. The disinfected water is removed from the outlet at the top of sterilizer. The disinfected water is colourless, odourless and tasteless.

Disinfection of municipal water supply is not done by ozone because it is an expensive method.

(E) *By Ultra-violet light*. UV-light is also used as a disinfectant. As no chemicals are used so this process is quite safe for human skin.

#### Ultraviolet Irradiation

The UV unit consists of one or more UV lamps usually enclosed in a quartz sleeve, around which the water flows. The quartz sleeve surrounding each lamp protects the lamp from the cooling action of water.

The bacterial killing effect of the lamp is reduced when the lamp temperature is lowered. Water passes in a relatively thin layer around the lamp since the germicidal action of UV irradiation depends on the intensity of the light, depth of



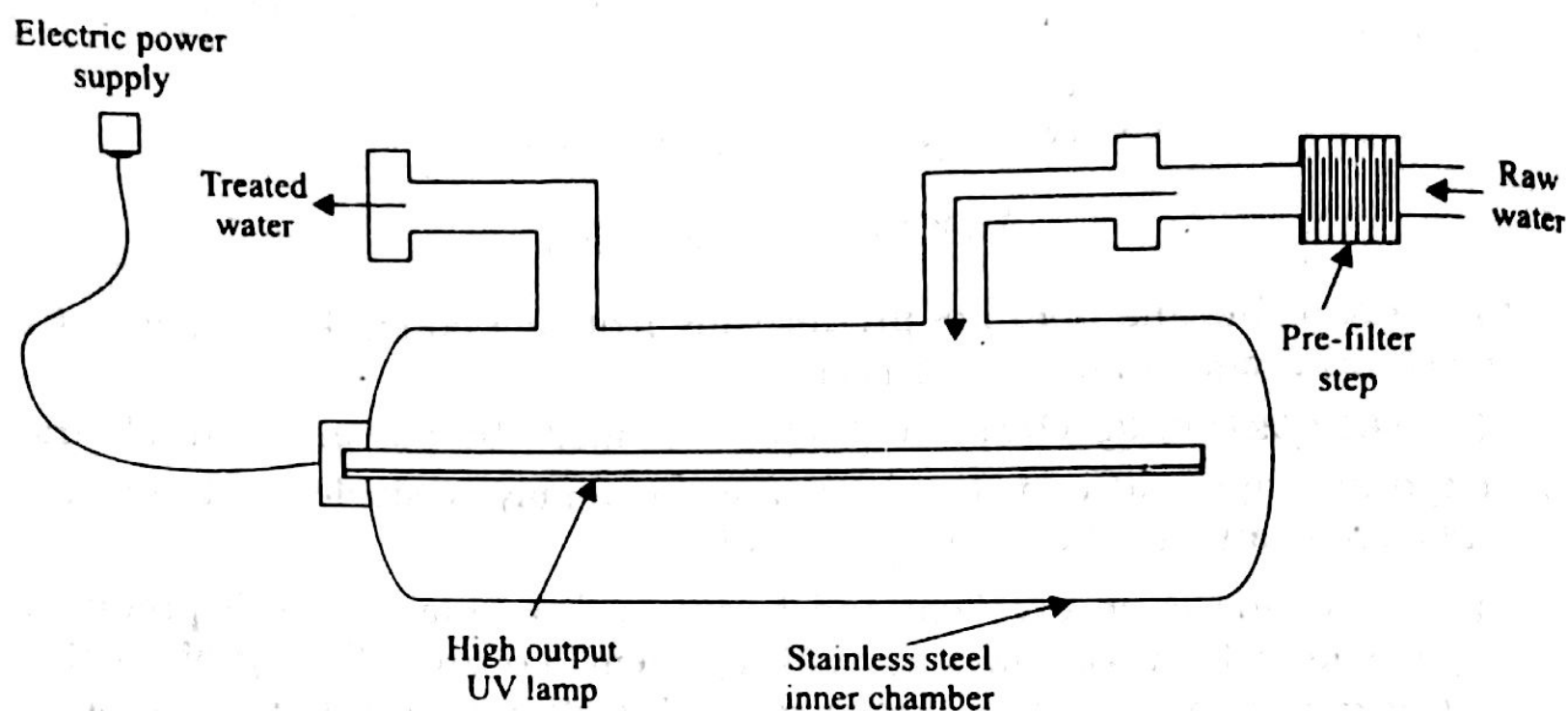


Fig. 31.

exposure, and contact time. Turbidity and minute traces of iron compounds reduce the light's transmission. Therefore, the water should be pre-filtered so that untreated organisms do not slip by.

#### Advantages

UV irradiation units are automatic, require little maintenance, and do not add undesirable materials to the water.

(F) *By potassium permanganate ( $\text{KMnO}_4$ )*.  $\text{KMnO}_4$  is very useful disinfectant especially for water of wells.

Table 14 : Comparison of Disinfectants

	Chlorine	Ozone	UV
1. pH range	Effective upto pH 7.5 ; less effective with higher pH values	pH independent ; but with pH above 8.5, the half life decreases rapidly leading to higher consumption	pH independent
2. Disinfection by-products	AOX, TriHaloMethane (THM*), Chlorate	THM and bromate possible	No by-products
3. Speed of disinfection	Slower than $\text{ClO}_2$	Fast	Fast
4. Stability of the disinfectant in the distribution system	Stable	No stability	No stability
5. Corrosivity	Corrosive	Corrosive	Not corrosive
6. Costs	Small investment costs, cheap product	High investment and maintenance costs	High investment and maintenance costs

**Table 15 : Comparison of the Advantages of Disinfection Methods**

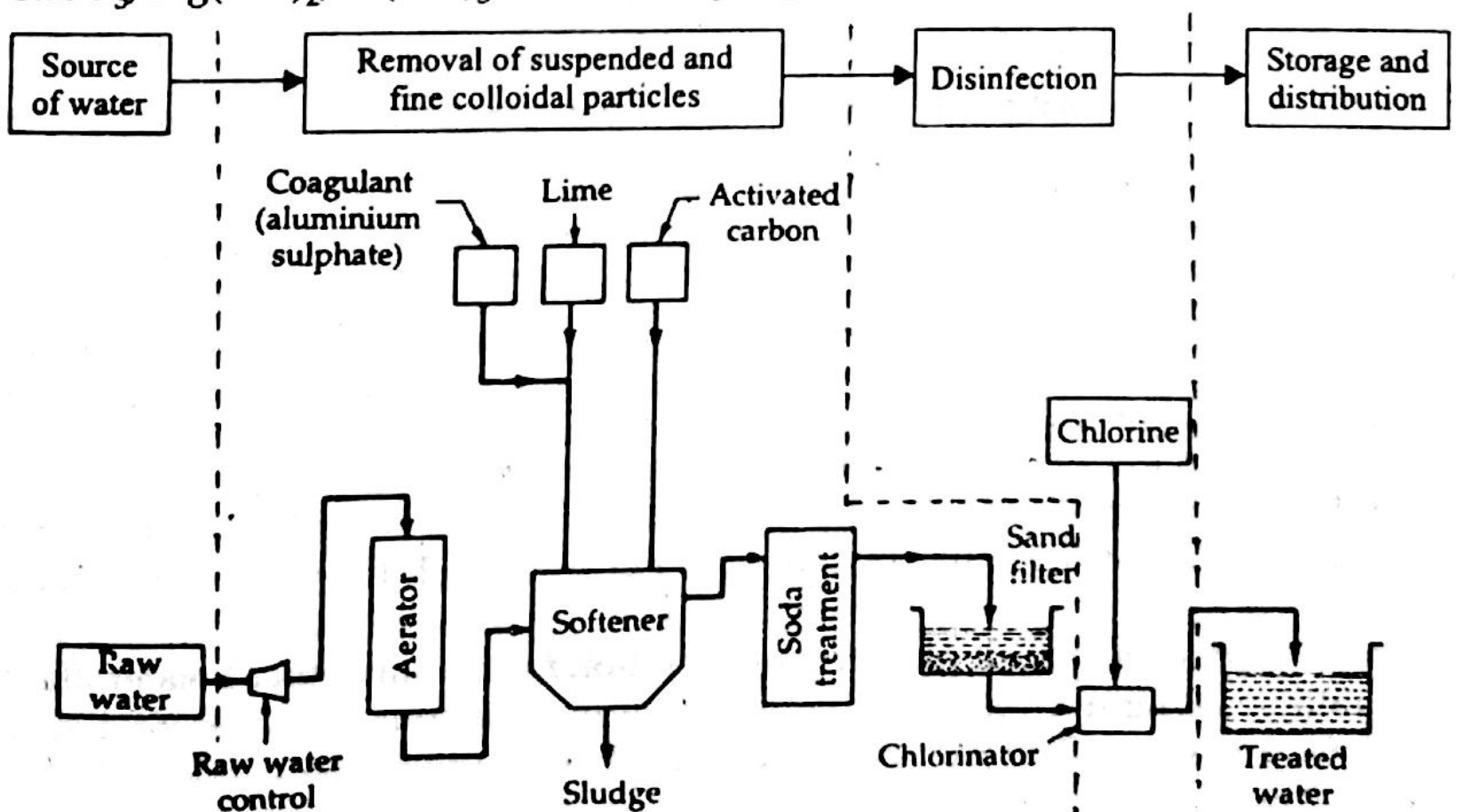
Criteria	Gas chlorine	Sodium hypo	Calcium hypo	Ozone	UV
1. Effective	Yes	Yes	Yes	Yes	Yes
2. Safe	No	No	No	?	Yes
3. Economical	Yes	?	No	No	No
4. Easy to use	?	?	?	?	?
5. Residual	Yes	Yes	Yes	No	No
6. Low TriHalo-Methane (THM) formation	No	No	No	Yes	Yes

**Treatment of ground water to be used for domestic purposes**

Before treating ground water, the nature as well as the amount of impurities present must be known.

Water from wells and springs (*i.e.*, Ground water or more specifically underground water) is generally free from suspended matter because of the filtration through porous strata. It is also rich in mineral salts. The possibility of contamination with toxic metals like Pb, As, Hg etc. is less but it is there. In that case, water is unfit for drinking or cooking purposes.

Because of the greater concentration of dissolved solids, the hardness in ground water is generally more than the prescribed limit of 85 ppm. In this case, water softening needs to be done. It can be effected either by precipitation and removal of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  in the form of their insoluble compounds (*viz.*,  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$  respectively) by using lime  $[\text{Ca}(\text{OH})_2]$  and

**Fig. 32. Flow sheet diagram showing municipal water treatment.**



soda ash ( $\text{Na}_2\text{CO}_3$ ) in *Lime-soda process*. The cations can also be replaced with ions such as  $\text{Na}^+$  via *Ion-exchange process*. A partial softening leaving a residual total-hardness of about 85 ppm (expressed as  $\text{CaCO}_3$ ) is usually adopted for drinking purposes. It is to be remembered that for drinking purposes, water should not be soft because soft water is plumbo-solvent (attacking lead used in plumbing).

After softening to prescribed limits, **disinfection** is done. Among the various disinfectants (like  $\text{Cl}_2$ , bleaching powder, ozone,  $\text{KMnO}_4$ , UV-light and  $\gamma$ -radiation) chlorine is most widely used.

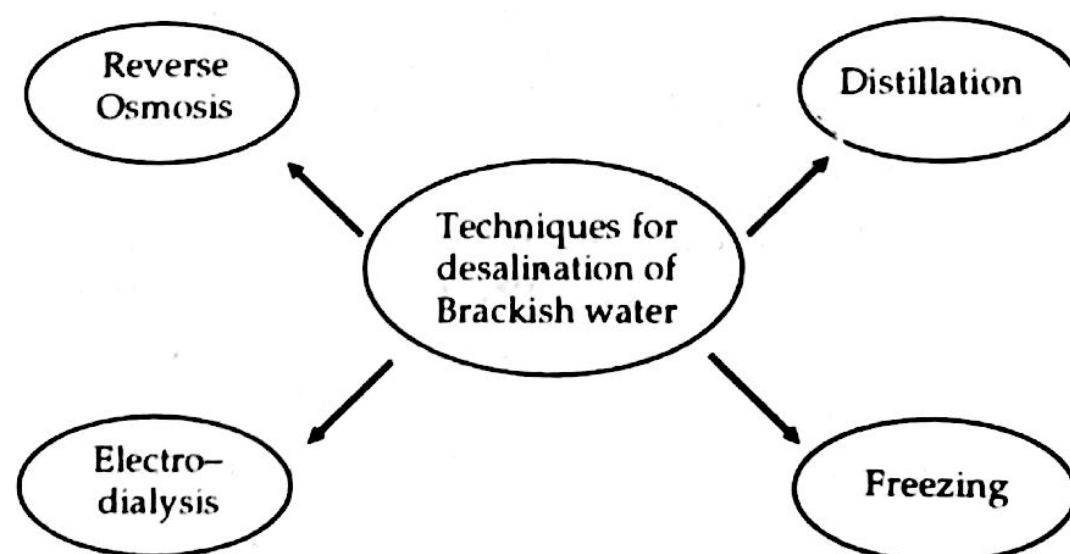
At this stage, water obtained will be fit for its use in domestic purposes.

To sum up, *municipal water treatment* can be illustrated by *flow diagram* shown in Fig. 32.

#### 14 DESALINATION OF BRACKISH WATER

Water containing high concentrations of dissolved solids with a peculiar salty or brackish taste is called *brackish water*. Sea water is an example for brackish water as it contains about 3.5% of dissolved salts. Before the removal of these salts, it is unfit for most of the domestic and industrial applications. The removal of dissolved solids ( $\text{NaCl}$ ) from water is known as *desalination process*.

Commonly used techniques for the desalination of brackish water are summarized in figure and discussed thereafter.



Techniques for desalination of Brackish water

(a) **Distillation.** Huge evaporators are used for boiling the brackish water and vapours collected are condensed to get pure water. It is an expensive method for common practice.

**Multiple effect evaporation for desalination of water.** Each unit or 'effect' in the '*multi-stage flash evaporators*' is maintained at a slightly lower temperature and pressure than the previous one in order to permit the steam produced in one unit, to become the source of heat in the next. At each unit, the water vapour condenses on condensers and the heat of condensation is utilized in heating the coils carrying the influent saline water. The condensed water from each flash chamber is collected. (Fig. 33)

In this process of multiple effect evaporation for desalination of water, flash evaporators having upto 50 stages have been used. Principle is simple, that is, to evaporate a part or all of the water from a saline solution and condensing the mineral-free water vapour.

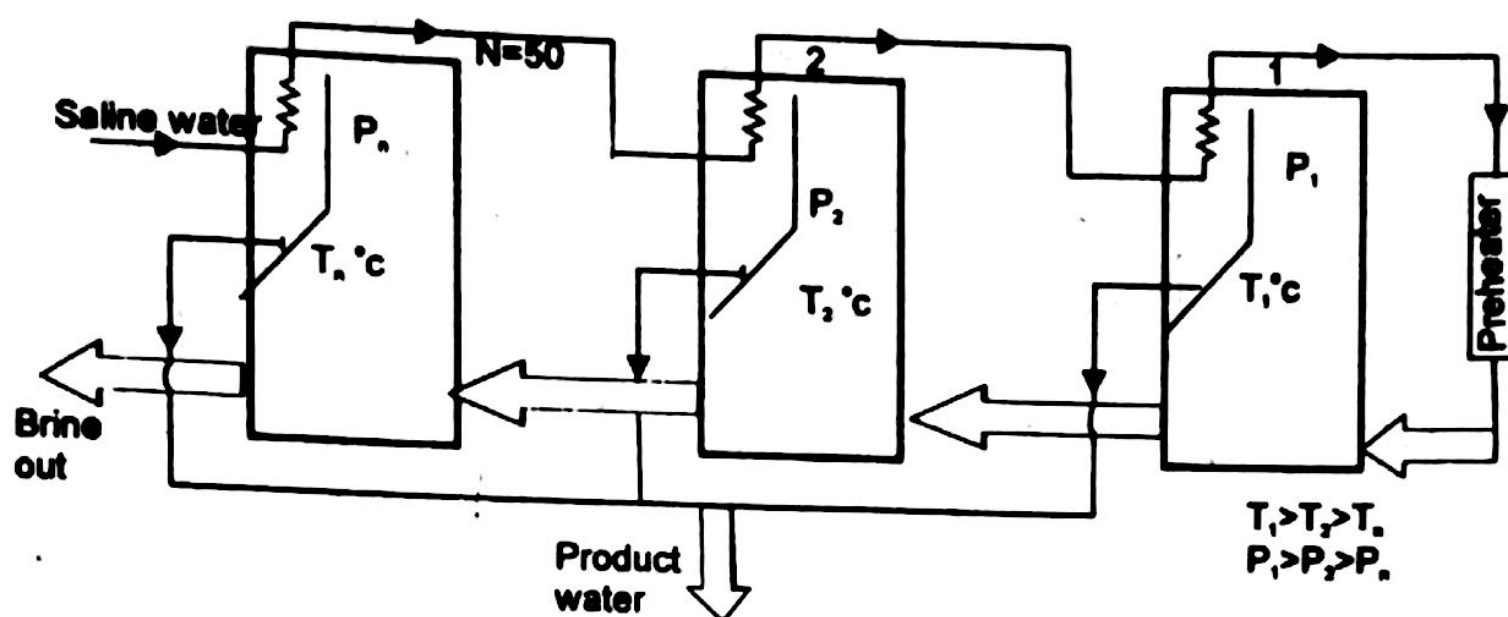


Fig. 33. Desalination of seawater by multistage flash evaporators.

**Desalination of sea water using a solar still.** Although distillation by solar energy has the advantage of 'free energy' but it requires large collectors in relation to the energy delivered. Obviously capital cost in this process is huge.

In this process, water is evaporated from a shallow black pan exposed to the sunlight and covered with sloping glass sheets. On these sheets, the evaporated water condenses and runs down to the collecting channels at the base of the covers. (Fig. 34)

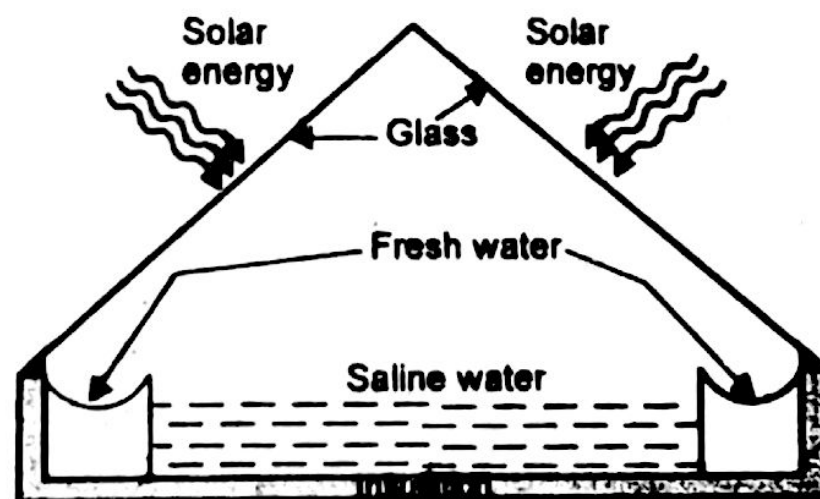


Fig. 34. Diagrammatic representation of desalination of sea water using a solar still.

Per day, about 73 kg of water can be produced per  $\text{m}^2$  of evaporator pan.

(b) **Freezing.** Salt can be separated from brackish water by freezing. This is because when brackish water is cooled, salt is left in the mother liquor and ice crystals are formed. These crystals can be easily separated, washed and melted to get pure water. This method can be practised only in cold climatic areas and is expensive also.

(c) **Electrodialysis.** Electrodialysis is based on the fact that the ions present in saline water migrate towards their respective electrodes, through ion-selective membranes (natural or synthetic) under the influence of applied emf.

The method of electrodialysis can be illustrated with the help of Fig. 35. The unit consist of electrodes (cathode and anode) and thin and rigid ion-selective membranes which are permeable to either cation or anion. The anode is placed near the anion-selective membrane while the cathode is placed near the cation-selective membrane. [The *anion selective membrane* is embedded with positively charged functional groups such as  $\text{R}_4\text{N}^+$  and is permeable to anions only. This is due to the



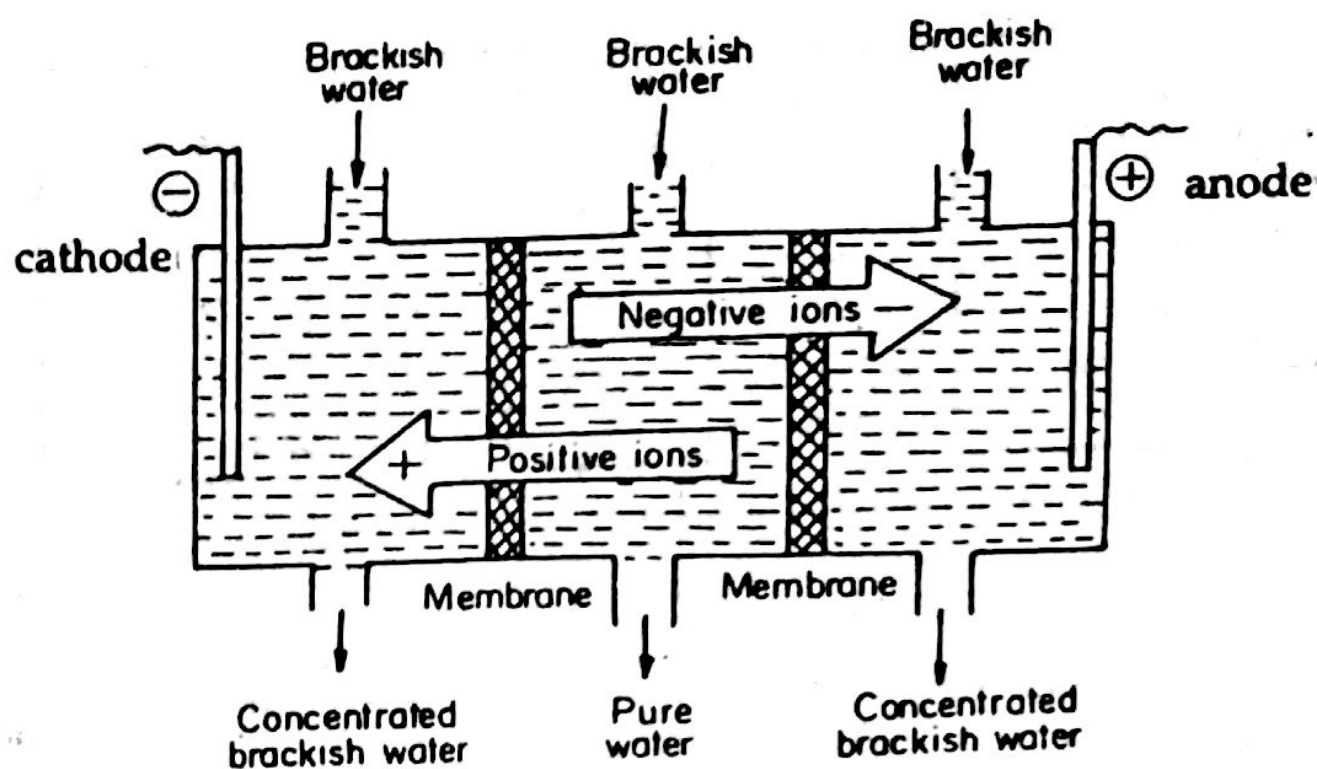


Fig. 35. Electrodesialysis of brackish water.

presence of fixed functional groups, which carry positive charge, inside the membrane. Similarly, a *cation selective membrane* is based on polystyrene resin embedded with negatively charged functional groups such as  $\text{RSO}_3^-$  or  $\text{RCOO}^-$  and is permeable only to cations, while anions stay away as they feel electrostatic repulsion]. Under the influence of an applied emf across the electrodes the cations ( $\text{Na}^+$ ) move towards the cathodes through cation selective membrane and anions ( $\text{Cl}^-$ ) move towards the anode through anion selective membrane (see Fig. 35) the net result is the depletion of ions in the central compartment while it increases in the two side compartments. Desalinated water is periodically drawn out from the central compartment while the concentrated brackish water is replaced by fresh samples.

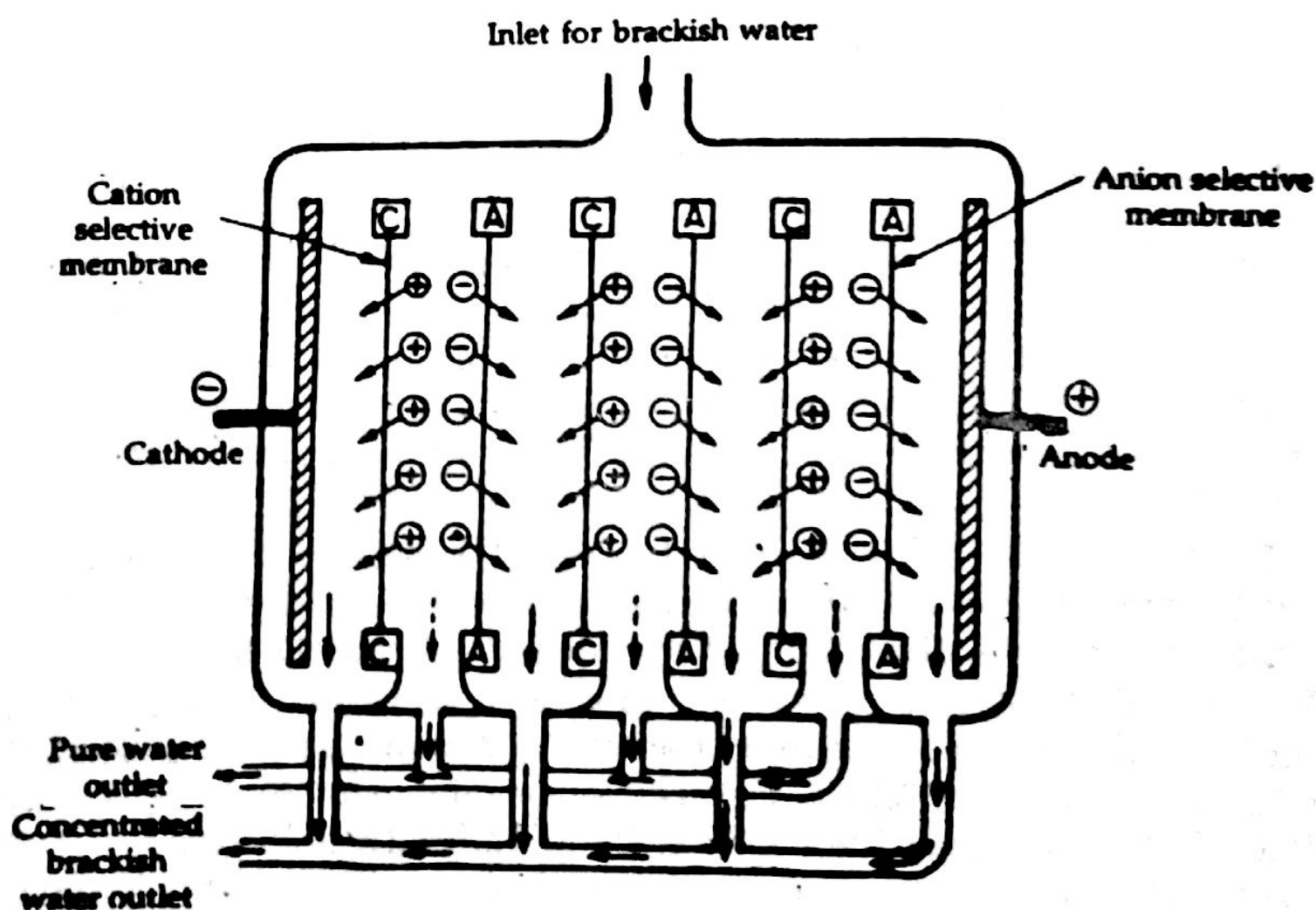


Fig. 36. Electrodesialysis cell.

For practical purposes, an electrodialysis cell is used. It consists of large number of paired sets of ion-selective membranes, see Fig. 36. Under a pressure of about  $5\text{--}6\text{ kg/m}^2$ , saline water is passed in and we get alternate streams of pure water and concentrated brackish water. The principle is similar to that discussed above.

**Electrodialysis** is an electrically-driven separation conducted at very low pressure-driven, size-exclusion filtering process.

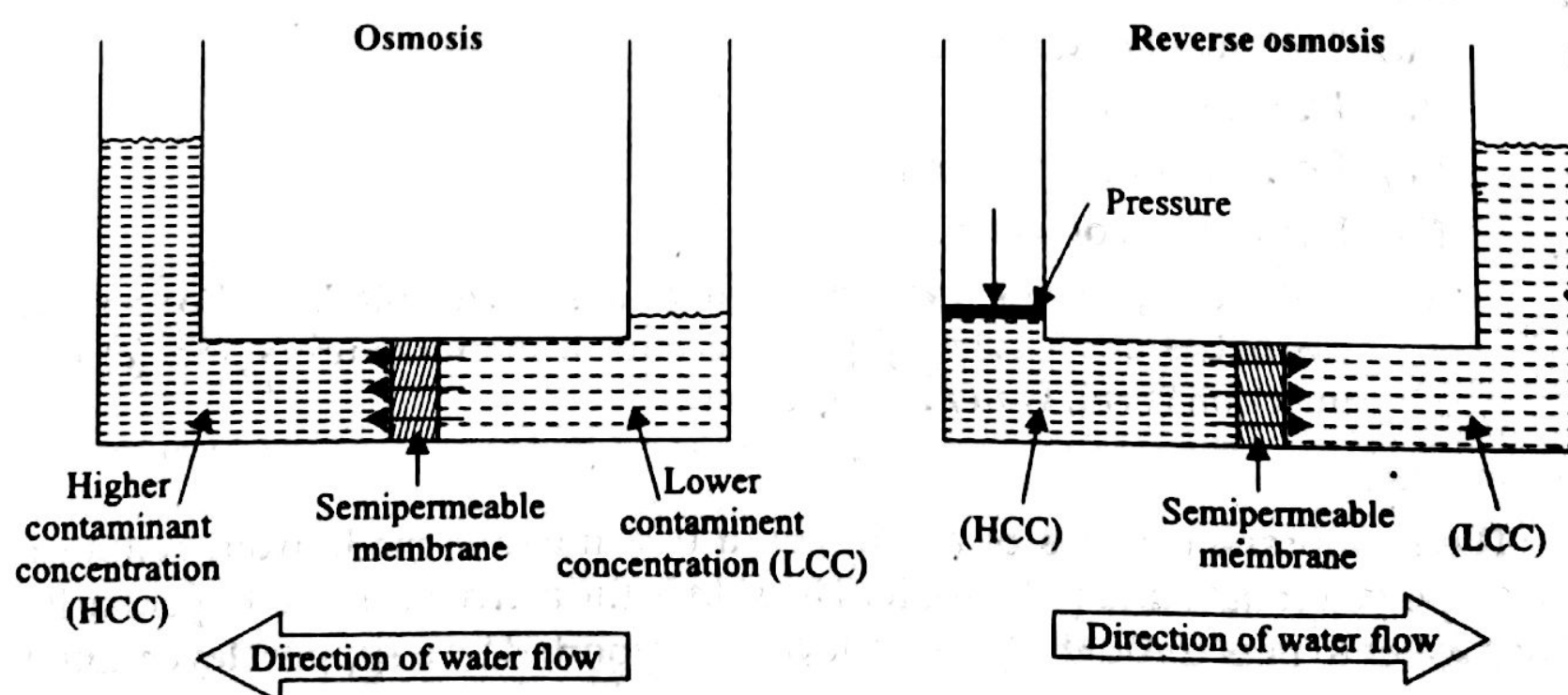
The ion-exchange membranes are electrically conductive and impermeable to water flow, even under pressure.

The **electrodialysis reversal (EDR)** process was introduced in the commercial sector to improve the electrodialysis process. The EDR process operates on the same principle as the conventional ED unit except at intervals of several times an hour, the polarity of the electrodes is reversed and the flows are simultaneously switched so that the brine channel becomes the product water channel and vice versa. The reversal feature is useful in breaking up films, scales, and other deposits and flushing them out of the process before they can build up and foul the membranes.

#### *Advantages of desalination by electrodialysis*

- (i) This process is economical as per the capital cost and operational expenses are concerned.
- (ii) The unit is compact and the method is best suited.

(d) **Reverse Osmosis.** Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane. (Semi-permeable membrane is selective membrane which does not permit the passage of dissolved solute particles.) The flow continues till the concentration is equal on both the sides. The driving force for osmosis is *osmotic pressure*. However, if a *hydrostatic pressure* in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis of *reverse osmosis*.



**Fig. 37.** Diagrammatic representation of desalination of sea water using a solar still.



For practical purposes, semi-permeable membrane based on thin films of cellulose acetate, polymethyl acrylate and polyamide polymers are used. A pressure of the order of  $15-40 \text{ kg/cm}^2$  is applied (Fig. 38) for separating the water (pure solvent) from its contaminants. The process is also known as *super-or hyper-filtration*.

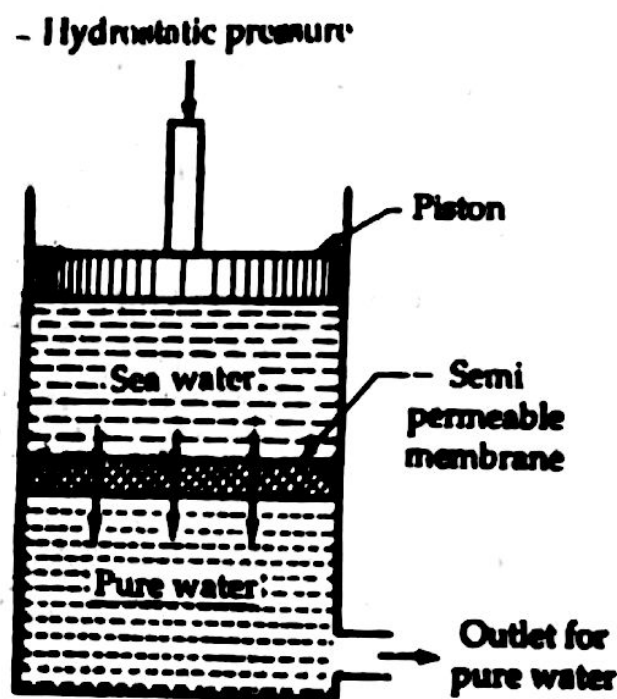


Fig. 38. Reverse Osmosis cell.

#### Advantages

- (i) Colloidal  $\text{SiO}_2$  can be removed by reverse osmosis which even cannot be removed by demineralisation ;
- (ii) It is simple and reliable process ;
- (iii) Capital and operating expenses are low ;
- (iv) The life of the semi-permeable membrane is about 2 years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.
- (v) It operates at a comparatively low temperature.
- (vi) It is relatively energy efficient.

#### Applications :

- (i) Treatment of waste water,
- (ii) Desalination,
- (iii) Reclamation of minerals,
- (iv) Purification of water,
- (v) In making processed water : (a) For dialysis in hospitals, (b) For certain cosmetics and drugs by pharmaceutical manufacturers and (c) For injection (WFI, water for injection).

#### RO Membrane

The membrane consists of a skin about 0.25 microns made from cellulose acetate, polysulfonate and polyamide. The skin is the active barrier and primarily allows water to pass through. The skin layer is supported by a support layer about 100 microns.

**Mechanism.** Water molecules can form hydrogen bonds in the RO membrane and fit into the membrane matrix. The water molecules that enter the membrane by hydrogen bonding can be pushed through under pressure. Most organic substances with a molecular weight over 100 are sieved out, *i.e.*, oils, pyrogens and particulates including bacteria and viruses. Salt ions, on the other hand, are rejected by a mechanism related to the valence of the ion. Ions are repelled by dielectric interactions, ions with higher charges are repelled to a greater distance from the membrane surface. Monovalent ions such as chloride ions will not be rejected as efficiently as, for example, divalent sulfate ions. The nominal rejection ratio of common ionic salts is 85 – 98%.

The amount of dissolved solids in water produced by RO is approximately a constant percentage of those in the feed water. For example, when the feed water contains 300 ppm total dissolved solids (TDS), the product water may have 15 to 30 ppm.

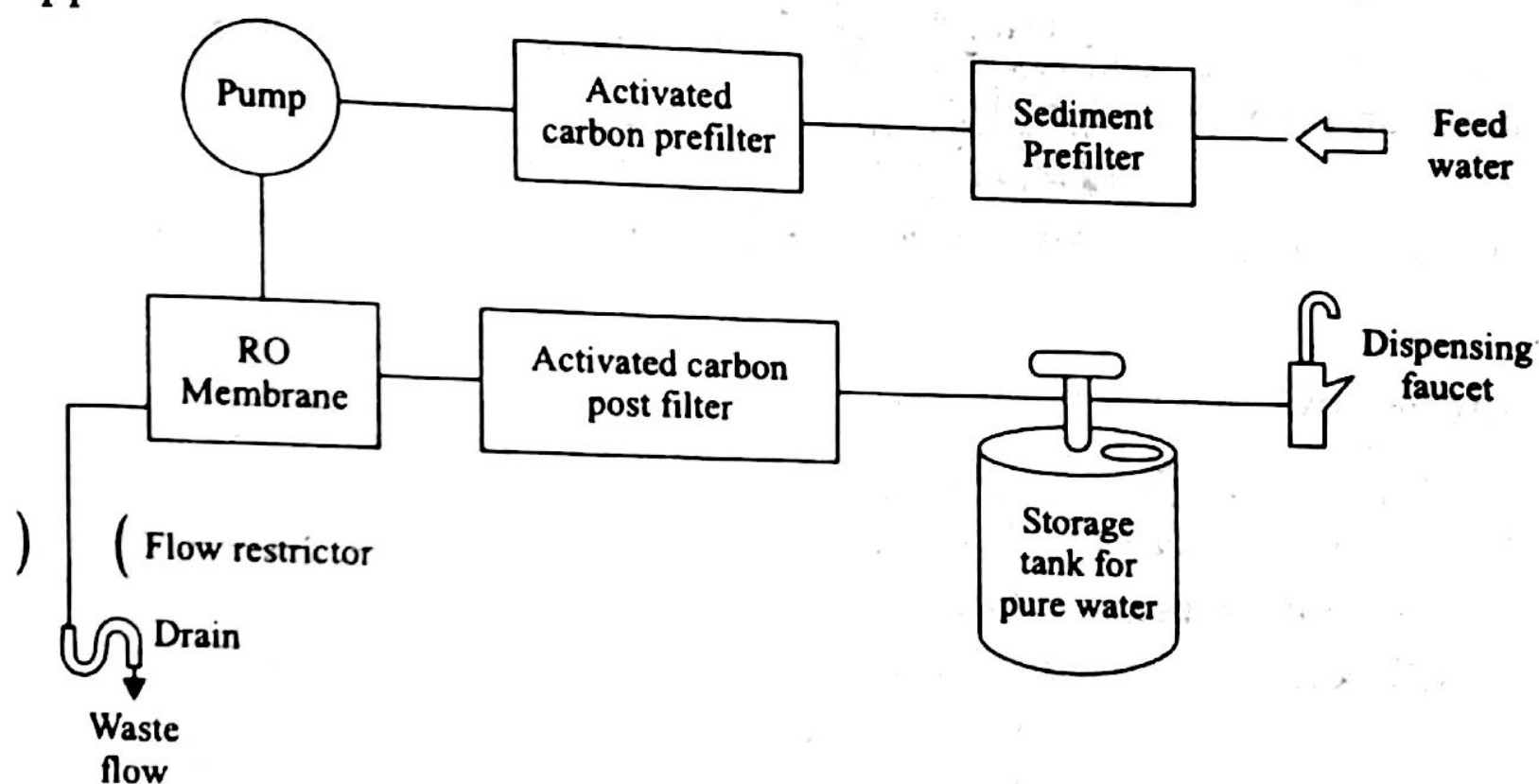


Fig. 39. The water softening process using Reverse Osmosis.

## 15 COOLING WATERS (Langeller Index)

One of the major applications of water in industry is for cooling purposes. Requirements of water used for cooling are :

- It should be non-scaling,
- It should be non-corrosive and
- It should be non-staining.

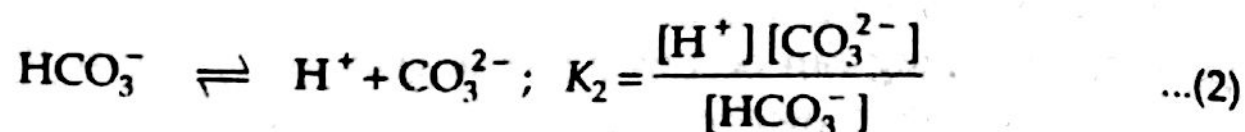
The knowledge of the **Langelier Index** ( $\text{CaCO}_3$  saturation index) helps in the prediction of the scaling or corrosive behaviour of natural waters. Water is said to be stable when it neither dissolves nor deposits  $\text{CaCO}_3$ . Such stable water will neither remove coatings of  $\text{CaCO}_3$  that may protect pipes against corrosion nor lay down deposits of  $\text{CaCO}_3$  that may clog pipes.

Let  $K_{sp}$  is the solubility product of  $\text{CaCO}_3$

$$\text{i.e., } K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \Rightarrow [\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Ca}^{2+}]} \quad \dots(1)$$



And  $K_2$  is the dissociation constant of the reaction



From equations (1) and (2),

$$[\text{H}^+] = \frac{K_2 [\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{K_2 [\text{HCO}_3^-]}{K_{sp}/[\text{Ca}^{2+}]} = \frac{K_2}{K_{sp}} [\text{HCO}_3^-] [\text{Ca}^{2+}]$$

$$\Rightarrow -\log [\text{H}^+] = -\log \left( \frac{K_2}{K_{sp}} \right) - \log [\text{HCO}_3^-] - \log [\text{Ca}^{2+}]$$

$$\Rightarrow (\text{pH})_s = \log (K_{sp}/K_2) - \log [\text{HCO}_3^-] - \log [\text{Ca}^{2+}] \quad \dots(3)$$

The Langelier Index (LI), is defined as the algebraic difference between the actual pH and the saturation pH.

$$\text{LI} = \text{pH} - (\text{pH})_s \quad \dots(4)$$

The saturation pH  $\{(\text{pH})_s\}$  is calculated by using the formula given in equation (3).

### Significance of Langelier Index (LI)

(A) If  $\text{LI} = 0$ , the water is stable, i.e., it neither deposits scales of  $\text{CaCO}_3$  nor dissolve thin protective coating of  $\text{CaCO}_3$ ;

(B) If LI is positive, then it indicates that water has scale-forming tendencies;

(C) If LI is negative, then it indicates that water has corrosive tendencies.

For cooling purposes, it is usual to adjust the value of LI to be between 0.6 to 1.0.

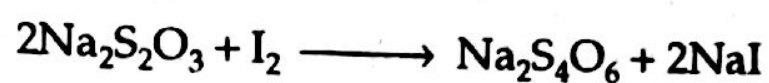
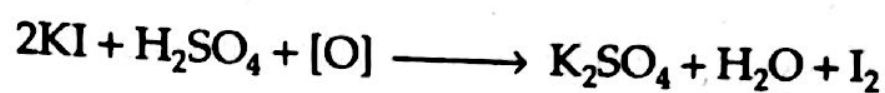
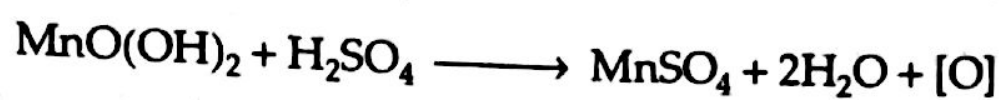
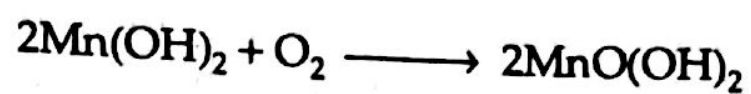
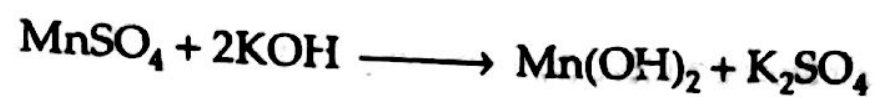
Sea water as a coolant is used only 'once-through' and then discharged to waste. However, cooling waters which are recirculated and used are usually subjected to cold lime process so as to remove only the carbonate hardness.

To avoid corrosion effects, chromates and dichromates are used as corrosion inhibitors in water used as coolant. Sludge (clay and sand) and algae often clog the condensers and heat exchangers. Periodic chlorination is done to counteract the growth of algae and mechanical methods are adopted to remove the sludge.

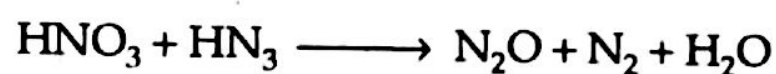
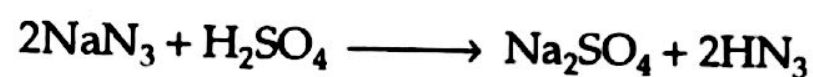
## 16 WATER ANALYSIS

### 16.1 Dissolved Oxygen

It is usually determined by *Winkler's method*. It is based on the fact that dissolved oxygen oxidises potassium iodide (KI) to iodine. The liberated iodine is titrated against standard sodium thiosulphate (also known as hypo) solution using starch as indicator. Since dissolved oxygen in water is in the molecular state, it as such cannot oxidise KI. Hence, manganese hydroxide is used as an oxygen carrier to bring about the reaction between KI and oxygen. Manganese hydroxide, in turn, is obtained by the action of KOH on manganese sulphate.



The oxidising agents present in water such as nitrate and ferric ions oxidize  $\text{I}^-$  to  $\text{I}_2$  and give positive error. To overcome this problem, sodium azide is used in alkaline iodide solution to decompose the nitrite or sulphite.



This is known as *Alsterberg's modification*.

The reducing agents like  $\text{Fe}^{2+}$ ;  $\text{SO}_3^{2-}$  or  $\text{S}^{2-}$  can reduce  $\text{I}_2$  to  $\text{I}^-$  and produce negative error. To overcome this problem,  $\text{KMnO}_4$  is used for pretreatment. Excess of  $\text{KMnO}_4$  is removed by reaction with potassium oxalate. This is known as *Rideat-stewart modification*.

**Procedure:** Take 250 mL of sample water in a bottle avoiding as far as possible contact with air. Immediately add 2 mL of manganous sulphate solution and 2 mL of alkaline KI solution. Stopper the bottle and shake them thoroughly. When the precipitate is settled, add 2 mL of conc. HCl and shake the bottle until the ppt has completely dissolved. Allow the yellow solution to stand for 5 minutes. Take 100 mL of this solution and titrate against N/100 hypo solution using starch as indicator. End point is the disappearance of blue colour. Let  $V_2$  mL of hypo solution is used.

$$\text{Normality of Hypo solution} = N_2 = \frac{1}{100} \text{ N}$$

$$\text{Volume of sample water taken for titration} = V_1 = 100 \text{ mL}$$

$$\therefore \text{Normality of sample water} = N_1 = \frac{N_2 V_2}{V_1} = \frac{\frac{1}{100} \times V_2}{100}$$

Since equivalent weight of  $\text{O}_2 = 8$

$$\text{Hence, strength of oxygen} = N_1 \times 8 \text{ gm/L}$$

$$= \frac{V_2}{10,000} \times 8 \text{ gm/L}$$

$$= \frac{V_2}{10,000} \times 8 \times 1000 \text{ mg/L}$$

$$\Rightarrow \text{Amount of dissolved oxygen} = 0.8 V_2 \text{ ppm.}$$



## 16.2 Biological Oxygen Demand (BOD)

Biological Oxygen Demand (BOD) is defined as the quantity of dissolved oxygen required by aerobic bacteria for the oxidation of organic matter under aerobic conditions.

The demand for oxygen is proportional to the amount of organic waste to be degraded aerobically. Hence, BOD approximates the amount of oxidizable organic matter present in the solution. When the BOD is high, the dissolved oxygen becomes low. Hence, greater the BOD, greater is the pollution. BOD is thus an indication of extent of pollution, this would be more clear from the BOD values of following effluents :

S.No	Source of effluent	BOD (ppm)
1.	Domestic sewage	320
2.	Cow shed sewage	3010
3.	Paper mill	8190
4.	Tannery effluent	12360

**Determination of BOD.** A known volume of effluent sample is diluted with a known volume of dilution water. The diluted sample is taken in two stoppered bottles. The dissolved oxygen content of one of the bottles is immediately determined (blank). Another bottle is incubated at 20°C for 5 days, after which unused oxygen is determined. The difference between the original oxygen content in the blank and unused oxygen of effluent water after 5 days gives the BOD.

Thus,  $BOD = (DO_b - DO_i) \times \text{Dilution factor}$

where BOD = Biological oxygen demand

$DO_b$  = dissolved oxygen present in the effluent sample before incubation (blank)  
and  $DO_i$  = dissolved oxygen present in the effluent sample after incubation

Dilution by water is necessary so as to make ensure that sufficient oxygen is available for the complete oxidation of organic matter, while carrying out the BOD test, seed ("microbial organism") may also have to be provided if necessary.

**Example 1.** A 50 ml of sample contains 840 ppm of dissolved oxygen. After 5 days the dissolved oxygen value becomes 230 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.

**Solution.**  $BOD = (DO_b - DO_i) \times \text{Dilution factor}$

$$= (DO_b - DO_i) \times \frac{\text{ml. of sample after dilution}}{\text{ml. of sample before dilution}}$$

$$= (840 - 230) \times \frac{80}{50} = 976 \text{ ppm}$$

BOD is the requirement of oxygen due to biodegradable organic matter only and is biological phenomenon carried out more or less under natural conditions that exist in the receiving waters.

BOD test is usually influenced by type of microorganisms, pH, presence of toxins, some reduced mineral matter and nitrification process.

**Significance of BOD.** The BOD values are very useful in process design and loading calculations, i.e., designing of treatment plants and calculations of waste load. BOD is a measure of efficiency of operation in treatment plant. In general, BOD gives a qualitative index of the organic substances which are degraded quickly in short period of time. From the BOD value, we can determine the self purifying capacity of streams which serves as a measure to assess the quantity of wastes which can be safely assimilated by the stream. BOD test is the best test for assessing the organic pollution. It serves as a guide-line for Regulatory Authorities to check the quality of effluents discharged into such water bodies.

**Limitations of BOD.** BOD values of effluents of rayon industries, paper and pulp industries and chemical industries are much less although they contain enough organic matter. The conclusion drawn from the low BOD value (that less organic matter is present) is wrong. Thus, BOD values should not be used as equivalent to organic load because of the presence of cellulose and other non-degradable organic matter.

In these cases, chemical oxygen demand reveals the real pollution potential.

### 16.3 Chemical Oxygen Demand (COD)

Chemical oxygen demand is defined as the amount of oxygen (expressed in mg/L or ppm) consumed under specified conditions in the oxidation of organic and oxidisable inorganic matter, corrected for the influence of chlorides.

In COD test, the sample is subjected to chemical oxidation with potassium dichromate ( $K_2Cr_2O_7$ ) which is a strong chemical oxidising agent than  $O_2$ . Thus oxidation of both biological oxidisable and biologically inert material in the effluent water sample takes place. Hence, COD value for sample is always higher than BOD value. Time required for COD test is short hence COD test is advantageous.

**COD determination.** A known volume (say 25 mL) of the waste water sample is refluxed for  $1\frac{1}{2}$  hours with a known excess of standard potassium dichromate (say 1 N) in a 50% sulphuric acid solution in the presence of silver sulphate ( $Ag_2SO_4$ ) as catalyst (to promote oxidation of straight chain aliphatic compounds, aromatic compounds and pyridine) and mercuric sulphate (to suppress chloride ion interference). The organic matter of the sample is oxidised to  $H_2O$ ,  $CO_2$  and  $NH_3$ . The excess dichromate remaining unreacted in the solution is titrated with a standard solution of ferrous ammonium sulphate,  $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$ . This experimentally measured amount of  $K_2Cr_2O_7$  (which is consumed) is used to calculate the equivalent oxygen required by the waste water for degradation of the pollutants.

Mathematically,

$$COD = \frac{(V_b - V_t) \times N \times 8}{V_s} \times 1000 \text{ mg/L}$$



where COD is chemical oxygen demand,  
 $V_b$  and  $V_t$  are the volumes of ferrous ammonium sulphate consumed in the blank and test experiments.  
 $N$  is normality of ferrous ammonium sulphate  
 and  $V_e$  is the volume of effluent sample taken.

**Example 2.** A 25 mL of a sewage water sample was refluxed with 10 mL of 0.25 N  $K_2Cr_2O_7$  solution in presence of dil.  $H_2SO_4$ ,  $Ag_2SO_4$  and  $HgSO_4$ . The unreacted dichromate required 6.5 mL of 0.1 N ferrous ammonium sulphate.

10 mL of the same  $K_2Cr_2O_7$  solution and 25 mL of distilled water, under the same conditions as the sample, required 27 mL of 0.1 N ferrous ammonium sulphate. Calculate the COD of the sewage water sample.

**Solution.** Given  $V_b = 27$  mL  
 $V_t = 6.5$  mL  
 $N = 0.1$  Normal  
 and  $V_e = 25$  mL

$$\therefore \text{COD} = \frac{(27 - 6.5 \times 0.1 \times 8)}{25} \times 1000 = 0.656 \text{ ppm}$$

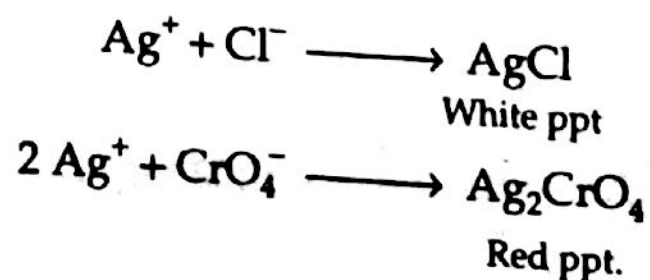
**Importance of COD.** The COD is another index of pollution which measures, the effect of pollutants on dissolved oxygen. COD value is not affected by the presence of toxins and other unfavourable conditions for the growth of microorganisms. Due to its rapid determination, COD is very important parameter in management and design of the treatment plants. COD values are taken as basis for calculation of efficiency of treatment plants. COD is important in proposing standards for discharging domestic and industrial effluents in various kinds of water.

**Limitations of COD.** COD value is a poor measure of strength of organic matter as oxygen also get consumed in the oxidation of inorganic matter such as nitrates, sulphates, reduced metal ions etc. Although cellulose can be oxidized by this method but some organic materials like benzene, pyridine and few other cyclic organic compounds do not get oxidized by this test. COD test does not differentiate between bio-inert and biodegradable materials. It also does not indicate the rate at which the biologically oxidisable material stabilize.

#### 16.4 Chlorides

The chlorides are estimated by titrating the water sample with standard solution of silver nitrate using potassium chromate as indicator (*Mohr's method*).

The solubility product of  $AgCl$  is lower than that of  $Ag_2CrO_4$ . Thus, so long the  $Cl^-$  ions are available the less soluble  $AgCl$  is precipitated; the  $Ag^+$  ions are not sufficient for  $Ag_2CrO_4$  to be precipitated. As soon as all the  $Cl^-$  ions have been precipitated, even a drop of  $AgNO_3$  added (in excess) gives a red precipitate of silver chromate ( $Ag_2CrO_4$ ).



**Procedure :** (1) Pipette out 100 mL of given  $\text{Cl}^-$  solution in conical flask add 1 mL of  $\text{K}_2\text{CrO}_4$  indicator.

(2) Slowly add  $\left(\frac{N}{50}\right) \text{AgNO}_3$  solution from the burette. Initially, white ppt. is obtained. Continue the addition of silver nitrate till permanent reddish brown colour is obtained. Let  $V_2$  mL of  $\text{AgNO}_3$  gets consumed till end point.

**Calculations :**

(Volume  $\times$  Normality) of  $\text{Cl}^-$  = (Volume  $\times$  Normality) of  $\text{AgNO}_3$

$$\therefore 100 \times N_1 = V_2 \times \frac{N}{50} \Rightarrow N_1 = \frac{V_2}{5000} N$$

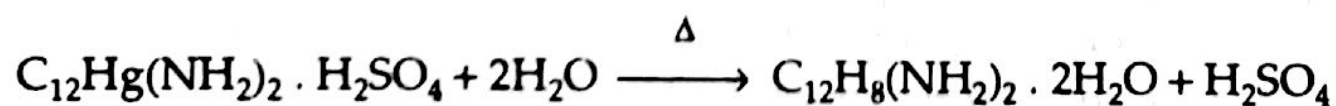
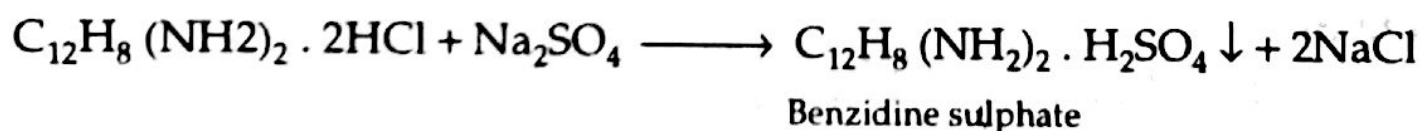
Strength of  $\text{Cl}^-$  ions =  $N_1 \times 35.5 \text{ gm/L} = N_1 \times 35.5 \times 1000 \text{ mg/L (or ppm)}$

$$= \frac{V_2}{5000} \times 35.5 \times 1000 = 7.1 V_2 \text{ ppm}$$

$\therefore$  Strength of  $\text{Cl}^-$  ions =  $7.1 V_2 \text{ ppm}$ .

### 16.5 Sulphates

The estimation of sulphate ions in water is based on their reaction with benzidine hydrochloride to form benzidine sulphate which is insoluble in cold and soluble in hot  $\text{H}_2\text{SO}_4$ .



The free sulphonic acid is then titrated against a standard  $\text{NaOH}$  solution using phenol phthalein as indicator.

**Procedure.** (a) Add 10 mL of benzidine hydrochloride solution to 100 mL of water sample.

(b) Mix the contents thoroughly and allow the precipitate to settle.

(c) With the help of whatmann filter paper (No. 4), filter the precipitate.

(d) Wash the ppt on filter paper with minimum of distilled water to free of acid.

(e) Transfer the ppt along with filter paper to a conical flask.

(f) Add 50 mL of distilled water to above flask and warm the contents to about  $50^\circ\text{C}$  to dissolve the precipitate.

(g) Titrate the liberated  $\text{H}_2\text{SO}_4$  against  $\text{NaOH}$  ( $N/50$ ) using phenolphthalein indicator (2-3 drops).

Let  $V_2$  mL of  $N/50$   $\text{NaOH}$  solution gets consumed till end pt.

**End point.** Appearance of permanent pink colour.



*Calculations :*

(Volume  $\times$  Normality) of  $\text{SO}_4^{2-}$  = (Volume  $\times$  Normality) of NaOH

$$\Rightarrow 100 \times N_1 = V_2 \times N/50$$

$$\Rightarrow N_1 = \frac{V_2}{5000} N$$

$\therefore$  Strength of  $\text{SO}_4^{2-}$  ions

$$= N_1 \times \frac{96}{2} \text{ gm/L} = N_1 \times 48 \times 1000 \text{ mg/L}$$

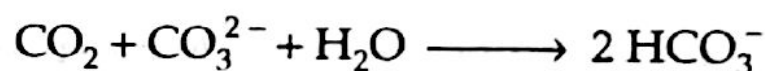
$$= N_1 \times 48 \times 1000 \text{ ppm}$$

$$= \frac{V_2}{5000} \times 48 \times 1000 \text{ ppm} = 9.6 V_2 \text{ ppm}$$

Hence strength of  $\text{SO}_4^{2-}$  ions =  $9.6 V_2$  ppm.

### 16.6 Dissolved $\text{CO}_2$

Carbon dioxide can be determined by titrating with a standard solution of  $\text{Na}_2\text{CO}_3$ . The estimation is based on the following reaction :



The completion of the reaction is indicated by the appearance of pink color by using phenolphthalein as indicator.

*Procedure :*

- In a 250 mL conical flask, pipette out 25 mL of given water sample.
- Add 2-3 drops of phenolphthalein indicator and titrate against N/50  $\text{Na}_2\text{CO}_3$  solution until the pink colour persists for at least 30 seconds. Take at least three concordant readings.
- Let V mL of N/50  $\text{Na}_2\text{CO}_3$  gets consumed till end point.

*End Point :* Appearance of pink colour which persists for at least 30 seconds.

*Calculations :*

(Volume  $\times$  Normality) of  $\text{CO}_2$  = (Volume  $\times$  Normality) of  $\text{Na}_2\text{CO}_3$

$$\Rightarrow (25 \text{ mL} \times N_1) = V \times \frac{1}{50}$$

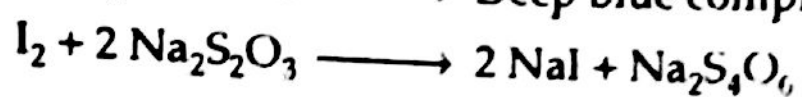
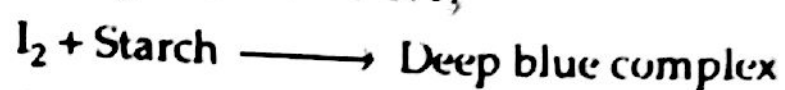
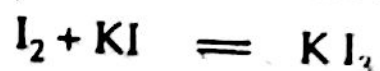
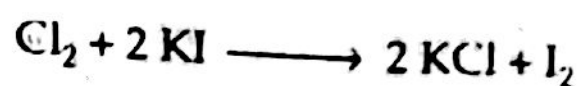
Therefore, Normality of the sample w.r.t.  $\text{CO}_2$  =  $N_1 = \frac{V}{50 \times 25}$

$$\text{Strength} = \frac{V}{50 \times 25} \times 22 \text{ gms/L} \times \frac{1000 \text{ mg}}{1 \text{ gm}}$$

or  $\text{free CO}_2 = \text{Strength} = 17.6 V \text{ mg/L}$

### 16.7 Free chlorine

Its estimation is based on the oxidation of potassium iodide by free chlorine, which liberates an equivalent amount of iodine. This liberated iodine is titrated with hypo solution using starch as indicator. End point is the disappearance of blue colour.



*Procedure.* (a) In a 250 mL stoppered conical flask, take about 10 mL of 10% KI solution.

(b) Stopper the flask and shake it vigorously.

(c) Remove the stopper and wash the adhering solution into flask, with about 5-10 mL of distilled water.

(d) Titrate this solution with N/50 Hypo solution using starch as indicator.

*End point :* Disappearance of blue colour.

*Calculations :*  $N_1 V_1$  of water sample =  $N_2 V_2$  of hypo solution

$$N_1 \times 50 = N/50 \times V_2$$

Hence, normality of (water sample or free chlorine) =  $\frac{V_2}{2500} N$

and strength of free chlorine =  $N_1 \times 35.5 \text{ gm/L}$

$$= \frac{V_2}{2500} \times 35.5 \times 1000 \text{ mg/L}$$

$\Rightarrow$  Strength of free chlorine =  $14.2 V_2 \text{ ppm}$ .

### 16.8 Total Dissolved Solids (TDS)

The dissolved solid content of a sample of water is important in deciding whether the water is suitable for boiler feed purposes. Dissolved solids denote mainly the various kinds of minerals present in water. However, some organic substances present in water also contribute to TDS.

It can be determined by evaporating an aliquot (100 mL) of the filtered sample to dryness and further heating the residue to constant weight at  $110^\circ \pm 10^\circ\text{C}$ . After cooling (in dessicator), the dish is weighed.

Total dissolved solids present in 100 mL of water

= weight of (dish + residue) – weight of dish

=  $w$  (gms.)

$$\therefore \text{TDS (in ppm)} = \frac{w}{100} \times 10^6 = 10^4 w \text{ ppm}$$

*Limitation :* During this heating, the bicarbonate ions are decomposed to give carbonate ions and gaseous  $\text{CO}_2$ , according to the equation :



The bicarbonate ions thus yield only carbonate ions.



**Solved Questions**

**Q. 1. Is it possible to remove permanent hardness by either boiling or adding lime alone ?**

**Ans. No.**

**Q. 2. Why is demineralization process preferred over zeolite process for softening of water for use in boilers ?**

*Or*

**Why is water softened by zeolite process unfit for use in boilers ?**

**Ans.** Because zeolite softened water contains large quantities of sodium salts like NaCl, Na<sub>2</sub>SO<sub>4</sub> etc., which can lead to caustic embrittlement.

**Q. 3. CO<sub>2</sub> should not be present in boiler feed water. Why ?**

**Ans.** Carbon dioxide forms carbonic acid (H<sub>2</sub>CO<sub>3</sub>). As the boiler wall material can be attacked slowly by carbonic acid and become weaker and weaker progressively, so CO<sub>2</sub> should not be present in boiler feed water.

**Q. 4. (a) What is meant by softening of water ?**

**(b) Why is water softened before using in boiler ?**

**Ans. (a)** Softening of water is the process of removing hardness-producing salts from water.

**(b)** Water should be properly softened before feeding it to boiler otherwise it may cause various boiler problems like

- (i) scale and sludge formation,
- (ii) boiler corrosion,
- (iii) priming and foaming etc.

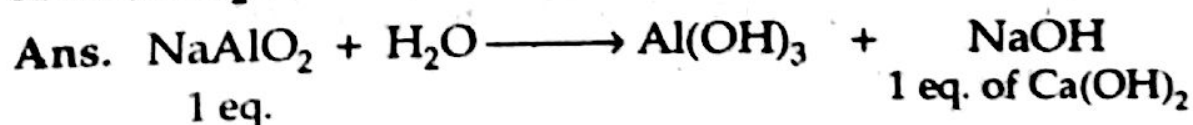
**Q. 5. Are coagulants also used in hot lime-soda process ? Give reasons.**

**Ans.** No, because reaction proceeds faster in hot lime-soda process and the precipitate and sludge formed settle down rapidly. Thus, no coagulants are required in hot lime-soda process.

**Q. 6. If silica is present in water, what harmful effects it can cause ?**

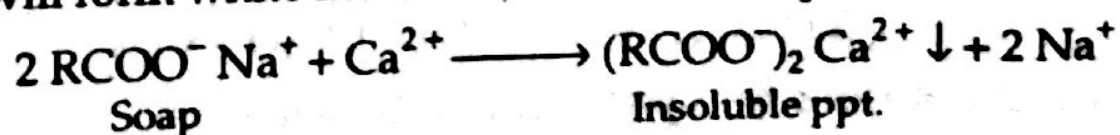
**Ans.** If silica is present in water, it causes the formation of very firmly sticking deposits of calcium silicate and magnesium silicate scales in the boiler which are very difficult to remove.

**Q. 7. Why is presence of NaAlO<sub>2</sub> in water equivalent to presence of equivalent of Ca(OH)<sub>2</sub> ?**



**Q. 8. If the water contains Ca<sup>2+</sup><sub>(aq)</sub> and HCO<sub>3</sub><sup>-</sup><sub>(aq)</sub> will it be hard water or soft water ? Give reason.**

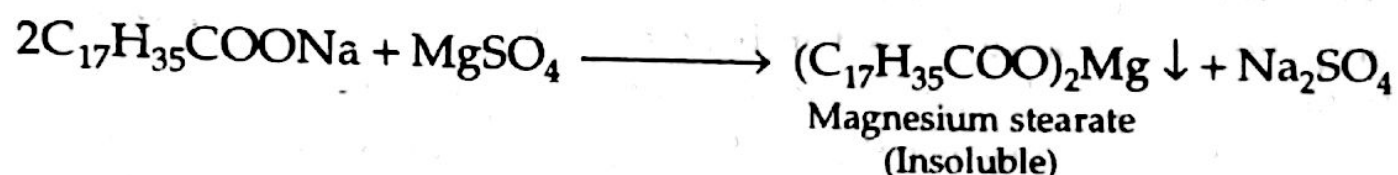
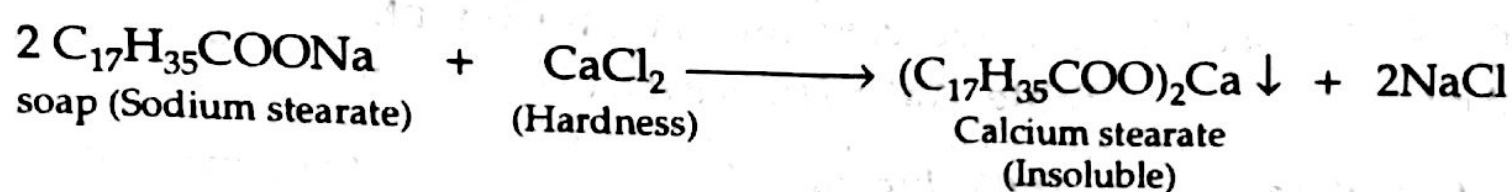
**Ans.** The given water is hard water. Because when such water is treated with soap solution, it will form white insoluble, scum, i.e., soap is not effective in it.



Moreover,  $\text{HCO}_3^-$  ions revert to  $\text{CO}_3^{2-}$  ions on heating and they form precipitate of  $\text{CaCO}_3$  by reacting with  $\text{Ca}^{2+}$  ions in boiler/kettles.

**Q. 9. Why does hard water consumes a lot of soap ?**

**Ans.** This is due to presence in water of certain salts of Ca, Mg and other heavy metal ions like  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  dissolved in it. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms insoluble white scum or precipitate which do not possess any detergent action. This is due to the formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are shown below :



**Q. 10. Why do we express hardness of water in terms of  $\text{CaCO}_3$  equivalent ?**

**Ans.** Although hardness of water is never present in the form of calcium carbonate because it is insoluble in water, hardness of water is conveniently expressed in terms of equivalent amount (*equivalents*) of  $\text{CaCO}_3$ .

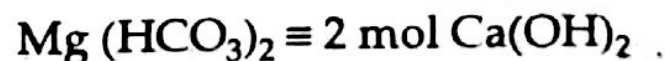
The reason for choosing  $\text{CaCO}_3$  as the standard for reporting hardness of water is the ease in calculations as its *molecular weight is exactly 100*. Moreover, it is the most insoluble salt that can be precipitated in water treatment.

**Q. 11. Why does magnesium bicarbonate require double amount of lime for softening ?**

**Ans.** Given hard water contains  $\text{Mg}(\text{HCO}_3)_2$  so for its softening we require lime, according to the equations :



Thus, from equation Requirement of lime for 1 mol

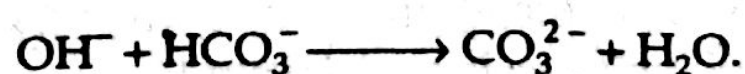


**Q. 12. Write the constituents responsible for the permanent hardness of water. Discuss one treatment method.**

**Ans.** Constituents responsible for permanent hardness are :  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ , etc.

**Q. 13. Give reasons why alkalinity of water cannot be due to the simultaneous presence of  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ .**

**Ans.** This is because,  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions react to form  $\text{CO}_3^{2-}$  ions according to :





**Q. 14.** 20 mL of a water sample was treated with excess of 10% KI solution and then titrated against N/100 hypo solution using starch as indicator. 2.5 mL of hypo was used for starch end point. Calculate the amount of chlorine in water.

**Ans.**  $N_1 V_1$  of water =  $N_2 V_2$  of hypo solution

$$\rightarrow N_1 \times 20 = \frac{N}{100} \times 2.5$$

Hence, normality of water sample having chlorine ( $N_1$ )

$$= \frac{1}{100} \times 2.5 \times \frac{1}{20} N = 0.0125 N$$

$\therefore$  Amount of chlorine in water =  $N_1 \times 35.5$  gms/L

$$= 0.0125 \times 35.5 = 0.444 \text{ gms/L}$$

**Q. 15.** Give a table as an overview for water treatment.

**Ans.**

**Table. Water Treatment (An overview)**

Constituent	Difficulties caused	Treatment method(s)
1. Suspended solids	Cause deposit in boilers, heat-exchangers, water lines etc.	Coagulation, settling and filtration.
2. Dissolved solids	Cause foaming in boilers, and process interference	Any softening method like lime-soda, zeolite or demineralization.
3. Turbidity	Imparts unsightly appearance to water, deposits in water lines, process equipment, etc.	Coagulation, settling and filtration.
4. Hardness	Forms curds with soap, interferes with dyeing, causes scale formation in boilers, heat-exchangers, pipelines etc.	Internal boiler water treatment, softening.
5. Alkalinity	Foaming and carry over of solids with steam, Embrittlement of boiler steel, carbonate and bicarbonate produce $\text{CO}_2$ in steam which causes corrosion in condensate lines.	Acid treatment ; softening.
6. Free mineral acids	Corrosion	Neutralization with alkalies.
7. Oxygen	Corrosion	Deaeration, sodium sulfite, corrosion inhibitors.
8. Carbon dioxide	Corrosion	Aeration, deaeration ; neutralization with alkalies.

**Q. 16.** Write a short note on water quality parameters.

**Ans.** The quality of water can be decided with the help of certain parameters named as water quality parameters.

These are : Colour, pH, Electrical conductivity, Turbidity, Suspended solids, Acidity, Alkalinity, Chlorides, Hardness, Sulphates, Dissolved oxygen, BOD, COD, Residual chloride, Chloride demand, Iron, Nitrogen and Phosphorus compounds, Fluoride and MPN (which indicates bacterial density).

**Q. 17. What is the advantage of reverse osmosis over ion-exchange process ?**

**Ans.** Apart from removing all ions, reverse osmosis also removes non-ionic, colloidal and high molecular weight organic matter.

**Q. 18. Why is calgon conditioning better than phosphate conditioning ?**

**Ans.** In calgon conditioning, the added calgon prevents scale and sludge formation in boiler because it forms soluble complex compound with calcium or magnesium ions. However, in phosphate conditioning, insoluble non-adherent precipitate of calcium phosphate is formed which then require the blow-down operation.

**Q. 19. Why is rain water a purest form of natural water ?**

**Ans.** Because rain water is obtained by the natural distillation process.

**Q. 20. Why is  $\text{NH}_3 - \text{NH}_4\text{Cl}$  buffer solution added during determination of hardness of water by EDTA method ?**

**Ans.** (i) Wine-red coloured metal-eriochrome black-T unstable complex formation,  
(ii) Colourless metal-EDTA stable complex formation, and  
(iii) Displacement of blue coloured free erio-chrome black-T indicator.

All these require basic medium ( $\text{pH} = 10$ ), maintained by the addition of  $\text{NH}_3 - \text{NH}_4\text{Cl}$  buffer.

### Exercises

- (i) Calgon treatment prevents scale formation in boilers, explain.  
(ii) Explain (in brief) boiler corrosion.
- (a) What is the principle of EDTA titrations ? How can the permanent hardness of water be determined by this method ?  
(b) Why is  $\text{NH}_3 - \text{NH}_4\text{Cl}$  buffer solution is added in determination of hardness of water by EDTA titration ?
- What are Zeolites ? How do they function in removing hardness of water ? What are the limitations of this process ?

Or

Explain with the help of a neat diagram, how can calorific value of a fuel be determined by Boy's calorimeter ?

- (a) One gm of  $\text{CaCO}_3$  was dissolved in dil HCl and solution diluted to one litre. 50 ml of this solution required 45 ml of EDTA solution, while 50 ml of sample water required 18 ml of EDTA solution. On the other hand, 50 ml of boiled sample water when titrated against EDTA consumed 9 ml of solution. Calculate each type of hardness in ppm.  
(b) Differentiate between scale and sludge.
- (a) How will you determine the alkalinity of water sample containing hydroxide and carbonate ion ?  
(b) A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 ml of water sample on titration with  $\frac{N}{50}$  HCl required 4.7 ml of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and the titration further continued, the yellow colour of the solution just turned red after addition of another 10.5 ml of the acid solution. Elucidate on the type and extent of Alkalinity present in the water sample.



6. (a) Give details of the following :
- (i) Scale and sludge formation                      (ii) Break Point Chlorination
- (b) Zeolite softners are not recommended for obtaining feed water for the modern high pressure boilers. Give reasons.
- (c) Why is calgon conditioning better than phosphate conditioning ?
- (d) Calculate the quantity of lime and soda required for cold softening of  $10^4$  litres of water using 139 ppm of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  as a coagulant. The results of the analysis of raw water and softened water are as follows :
- | <i>Raw water</i>                          | <i>Softened water</i>                |
|---|--------------------------------------|
| $\text{Mg}^{2+} = 48 \text{ ppm.}$        | $\text{CO}_3^{2-} = 60 \text{ ppm.}$ |
| $\text{Ca}^{2+} = 200 \text{ ppm.}$       | $\text{OH}^- = 17 \text{ ppm.}$      |
| $\text{HCO}_3^- = 488 \text{ ppm.}$       |                                      |
| Dissolved $\text{CO}_2 = 44 \text{ ppm.}$ |                                      |
| Free $\text{HCl} = 71 \text{ ppm.}$       |                                      |
7. (a) What do you mean by Priming and Foaming ? How does it take place in boilers ?
- (b) Describe the ion exchange process of water softening.
- (c) 0.28 g of  $\text{CaCO}_3$  was dissolved in  $\text{HCl}$  and the solution was made upto 1 litre with distilled water, 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of Hard water sample required 33 ml of same EDTA solution on titration. After boiling 100 ml of this water cooling, filtering and then titration required 10 ml of EDTA solution. Calculate carbonate and non carbonate hardness of given sample of water in terms of ppm.
8. (a) Explain with equations and calculate the quantity of lime and soda required to soften 10,000 L of water containing
- $\text{Mg}(\text{HCO}_3)_2 = 219 \text{ ppm, NaCl} = 234 \text{ ppm, Mg}^{2+} = 36 \text{ ppm, HCO}_3^- = 18.3 \text{ ppm, H}^+ = 15 \text{ ppm, SO}_4^{2-} = 144 \text{ ppm, Cl}^- = 71 \text{ ppm}$
- (b) What happens when temporary hard water is boiled ? (Give Equations)
- Or
- Write short notes on : (i) Zeolite or Permutit process ; (ii) Scale formation in Boilers.
9. (a) What are complexometric titrations ?
- (b) Explain the principle of EDTA titrations.
- (c) Is it necessary to maintain the pH of the solution nearly constant by adding a suitable buffer during EDTA titrations ?
- (d) Describe the process of estimation of Ca and Mg with EDTA.
- (e) Write the structures of :
- (i) Metal-EDTA complex ;                      (ii) Eriochrome black-T indicator.
10. Explain : Buffer solution ; Buffer action ; Buffer capacity ; Acidic and Basic Buffer solution.

### Short Answer Type Questions

#### 1. Based on hardness

11. Is it possible to remove permanent hardness by either boiling or adding lime alone ?
12. If the water contains  $\text{Ca}^{2+} (\text{aq})$  and  $\text{HCO}_3^- (\text{aq})$  will it be hard water or soft water ? Give reason.

13. Why do we express hardness of water in terms of  $\text{CaCO}_3$  equivalents?
14. Why water should not be soft for drinking purposes?
15. Why do we use buffer solution in EDTA titrations?

## II. Based on EDTA method of Hardness Determination

16. Why water should be free from  $\text{SiO}_2$ , if it has to be used for paper industry?
17. What is the principle of EDTA titrations?
18. What is the advantage of EDTA method?
19. What is the significance of hardness determination?
20. What is the limitation of EBT? How is it overcome?

## III. Based on Alkalinity

21. Why a given water sample cannot be alkaline due to the simultaneous presence of  $\text{OH}^-$  and  $\text{HCO}_3^-$  ions?
22. What do you mean by alkalinity of water?
23. What are the drawbacks of using highly alkaline water?
24. How will you conclude that a given water sample is alkaline due to simultaneous presence of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions?
25. How alkalinity is calculated if a given water sample is alkaline due to the presence of  $\text{HCO}_3^-$  ions only?

## IV. Based on Water Treatment Processes

26. Why it is desirable to remove temporary hardness before subjecting the raw water for softening to zeolite process?
27. If mineral acids are present in water, which method you will prefer for water treatment: Zeolite process or Ion-exchange process?
28. Why Zeolite process and ion-exchange processes are not suitable for the treatment of turbid water?
29. If it is desired to have water with residual hardness of: (a) 0 – 2 ppm, (b) 0 – 15 ppm, and (c) 15 – 50 ppm, then which external water treatment method will be suitable for each case?
30. What is the selection criteria for choosing an appropriate phosphate salt in phosphate conditioning?

## Objective Questions

### (A) Multiple Choice Questions

1. Which ion is not there in naturally occurring zeolite:  
(a)  $\text{Na}^+$                       (b)  $\text{Al}^{3+}$                       (c)  $\text{Si}^{4+}$                       (d)  $\text{Ca}^{2+}$
2. Which one, out of following is not a cation exchanger  
(a) Amberlite                      (b) Dowex                      (c) Duolite                      (d) Zeokarb  
(e) none
3. Plumbosolvency is a health hazard in the transportation of:  
(a) soft water only                      (b) Hard water only  
(c) both (a) and (b)                      (d) none of (a) and (b)



4. Which of the following dissolved salts in water would cause the least hardness in water sample ?  
(a) 10 ppm of  $\text{CaSO}_4$  (b) 10 ppm of  $\text{CaCO}_3$   
(c) 10 ppm of  $\text{MgCl}_2$  (d) 22.5 ppm of  $\text{Mg(OH)}_2$
5. Brackish water mostly contains  
(a)  $\text{CaCl}_2$  (b)  $\text{BaSO}_4$  (c)  $\text{NaCl}$  (d)  $\text{HCl}$
6. Ultraviolet rays are used in water treatment for  
(a) Sterilization (b) Coagulation (c) Sedimentation (d) Filtration
7. Chlorine is used in purification of drinking water for :  
(a) Coagulation (b) Desalination (c) Sterilization (d) none of these
8. The most ideal disinfectant in water treatment is :  
(a) Chloramine (b) Chlorine (c) Bleaching powder (d) All these
9. Potable water treatment does not involve :  
(a) Softening (b) Sedimentation (c) Coagulation (d) Disinfection
10. Colloidal conditioning of boiler is done by using  
(a) Calgon (b) Lignin (c) EDTA (d)  $\text{Na}_2\text{HPO}_4$
11. A sample of water contains sodium chloride. It is :  
(a) Soft water (b) Hard water (c) Moderately hard (d) none
12. Desalination is a process of removing :  
(a) oil (b) Common salt  
(c) Mineral acids (d) Hardness from water
13. Internal treatment of boiler-feed water involves :  
(a) To precipitate the scale forming substances in the form of sludge  
(b) To convert them into soluble substances  
(c) Both (a) and (b)  
(d) none of (a) and (b)
14. Temporary hardness in water can be removed by :  
(a) Boiling (b) Filtration (c) Sedimentation (d) Sterilization
15. Coagulants help in settling of :  
(a) Fine suspended impurities only  
(b) Suspended impurities only  
(c) Colloidal particles only  
(d) Both the suspended & colloidal particles
16. Potable water treatment does not involve :  
(a) Demineralisation (b) Disinfection (c) Coagulation (d) Sedimentation
17. Calgon is :  
(a)  $\text{Na}_3\text{PO}_4$  (b)  $\text{NaCl}$  (c)  $(\text{NaPO}_3)_6$  (d)  $\text{NaH}_2\text{PO}_4$
18. The flow of water through a membrane from saline water into fresh water takes place when the applied pressure on saline water is :  
(a) higher than osmotic pressure (b) lower than osmotic pressure  
(c) equal to osmotic pressure (d) zero
19. The coefficient of thermal expansion of boiler scale is :  
(a) Same as that of boiler plate (b) Less than that of boiler plate  
(c) Higher than of boiler plate (d) None of these

20. Alkalinity in water cannot be due to the presence of  
 (a)  $\text{OH}^-$  only  
 (b)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$   
 (c)  $\text{OH}^-$  and  $\text{HCO}_3^-$   
 (d)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$

### I. Based on hardness

21. Which salt among the following does not contribute towards temporary hardness :  
 (a) Calcium bicarbonate  
 (b) Magnesium bicarbonate  
 (c) Aluminium bicarbonate  
 (d) Calcium chloride
22. Which salt among the following does not contribute towards permanent hardness :  
 (a) Sodium bicarbonate  
 (b) Ferrous sulphate  
 (c) Aluminium sulphate  
 (d) Calcium sulphate
23. If a water sample contains 204 mg of  $\text{CaSO}_4$  per litre, its hardness (in ppm) in terms of  $\text{CaCO}_3$  equivalents will be :  
 (a) 150  
 (b) 160  
 (c) 170  
 (d) 140
24. The incorrect inter-relation among the following is :  
 (a) 1 ppm = 1 mg/L  
 (b) 1 ppm = 0.1 °Fr  
 (c) 1 ppm = 0.07 °Cl  
 (d) 1 ppm = 10 °Fr
25. The incorrect property of standard titrant used for hardness estimation among the following is :  
 (a) It is disodium dihydrate salt of EDTA  
 (b) It is a primary standard  
 (c) It is water soluble  
 (d) It is bi-dentate ligand.

### II. Based on EDTA method of Hardness Determination

26. The number of co-ordination sites in EDTA are :  
 (a) 1  
 (b) 2  
 (c) 4  
 (d) 6
27. Metal-EBT complex has wine-red colour at pH of  
 (a) 10  
 (b) 12  
 (c) 8  
 (d) 7
28. The colour of Metal-EDTA complex is  
 (a) Red  
 (b) Blue  
 (c) Black  
 (d) Colourless
29. EBT is  
 (a) Metal-ion indicator  
 (b) Acid-base indicator  
 (c) Both (a) and (b)  
 (d) None
30. The structure of metal-EDTA complex is  
 (a) Octahedral  
 (b) Trigonal planar  
 (c) Tetrahedral  
 (d) hexagonal

### III. Based on Alkalinity

31. If  $P = 0$ , the water sample is alkaline due to the presence of  
 (a)  $\text{OH}^-$   
 (b)  $\text{CO}_3^{2-}$   
 (c)  $\text{HCO}_3^-$   
 (d)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$   
 (e)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$
32. If  $P = M$ , the water sample is alkaline due to the presence of  
 (a)  $\text{OH}^-$   
 (b)  $\text{CO}_3^{2-}$   
 (c)  $\text{HCO}_3^-$   
 (d)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$   
 (e)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$



33. If  $P = M/2$ , the water sample is alkaline due to the presence of  
 (a)  $\text{OH}^-$  (b)  $\text{CO}_3^{2-}$  (c)  $\text{HCO}_3^-$  (d)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$   
 (e)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$
34. If  $P > M/2$ , the water sample is alkaline due to the presence of  
 (a)  $\text{OH}^-$  (b)  $\text{CO}_3^{2-}$  (c)  $\text{HCO}_3^-$  (d)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$   
 (e)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$
35. If  $P < M/2$ , the water sample is alkaline due to the presence of  
 (a)  $\text{OH}^-$  (b)  $\text{CO}_3^{2-}$  (c)  $\text{HCO}_3^-$  (d)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$   
 (e)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$

#### IV. Based on Water Treatment Processes

26. The amount of lime (in ppm) required for the softening of 10 litres of hard water containing 120 ppm of  $\text{MgSO}_4$  is :  
 (a) 740 (b) 750 (c) 730 (d) 760
27. The amount of soda (in ppm) required for the softening of 10 litres of hard water containing 24 ppm  $\text{Mg}^{2+}$  and 122 ppm  $\text{HCO}_3^-$  ions is :  
 (a) 0 (b) 20 (c) 40 (d) - 20
28. If the thickness of scale in boiler wall is 2.5 mm then the percentage wastage of fuel will be :  
 (a) 80 (b) 70 (c) 60 (d) 90
29. Which chemical is most suitable for the removal of calcium sulphate scale :  
 (a) EDTA (b)  $\text{HCl}$  (c)  $\text{HI}$  (d) EBT
30. For the removal of dissolved oxygen, which one is an ideal chemical :  
 (a) Hydrazine (b) 40% aqueous hydrazine solution  
 (c) Calculated quantity of b (d)  $\text{Na}_2\text{S}$

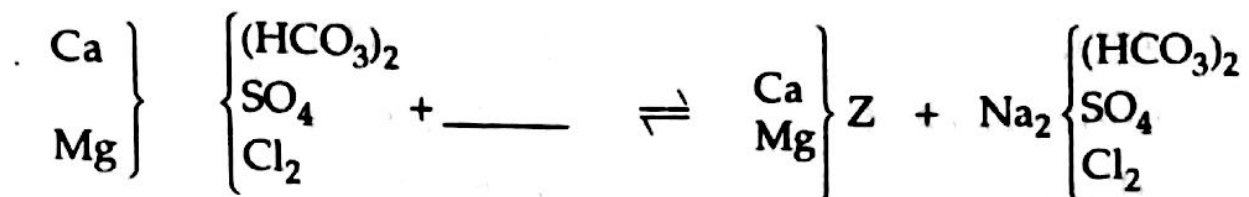
#### Answers

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (d)  | 2. (e)  | 3. (a)  | 4. (a)  |
| 5. (c)  | 6. (a)  | 7. (c)  | 8. (b)  |
| 9. (a)  | 10. (b) | 11. (a) | 12. (b) |
| 13. (c) | 14. (a) | 15. (d) | 16. (a) |
| 17. (c) | 18. (a) | 19. (b) | 20. (c) |

#### (B) Fill In The Blanks

- For efficient disinfectant action a greater concentration of \_\_\_\_\_ than of free chlorine residual is required.
- Chlorination of water to the extent of converting all the  $\text{NH}_3$  into  $\text{NCl}_3$  or  $\text{N}_2$  is referred to as \_\_\_\_\_.
- The removal of hardness-causing constituents such as the salts of Ca and Mg is called \_\_\_\_\_.
- The carbonate hardness is more effectively and economically removed by the \_\_\_\_\_(a)\_\_\_\_\_ process while the ion-exchange method is more economical in removing the \_\_\_\_\_(b)\_\_\_\_\_ hardness.

5. The exchange of ions of like sign between a solution and insoluble solid in contact with it is called \_\_\_\_\_.
6. In zeolite softening (let Z represents the zeolite framework)



7. \_\_\_\_\_ form scales on the hot surface of a boiler and sludges in the cooler regions.
8. Chlorine on adding to water produce \_\_\_\_\_ acid, which is a powerful germicide.
9. In phosphate conditioning, if the boiler feed water is too alkaline, \_\_\_\_\_ phosphate is used for internal conditioning.
10. Priming and foaming in boilers produce \_\_\_\_\_ steam.
11. Cation exchange resins contain \_\_\_\_\_ mobile ions.
12. The presence of residual \_\_\_\_\_ in boiler water causes caustic embrittlement.
13. The exhausted anion exchangers can be regenerated by working with \_\_\_\_\_.
14. Hydrazine hydrate is added in water to remove \_\_\_\_\_.
15. Hardness of water is expressed in terms of equivalent of \_\_\_\_\_.

### Answers

- |                               |                                 |
|-------------------------------|---------------------------------|
| 1. Combined chlorine residual | 2. Breakpoint chlorination      |
| 3. Water softening            | 4. (a) L – S, (b) non-carbonate |
| 5. Ion-exchange               | 6. $\text{Na}_2\text{Z}$        |
| 8. Hypochlorous               | 9. $\text{NaH}_2\text{PO}_4$    |
| 11. $\text{H}^+$              | 12. $\text{NaOH}$               |
| 14. Dissolved $\text{O}_2$    | 15. $\text{CaCO}_3$             |
|                               | 10. wet                         |
|                               | 13. Alkali solution             |

### (c) Match The Following

- |    |   |  |
|----|---|--|
| 1. | <b>A</b>                                  | <b>B</b>                                       |
|    | (i) Soft water                            | (a) > 180 ppm hardness                         |
|    | (ii) Moderately hard water                | (b) 121 – 180 ppm hardness                     |
|    | (iii) Hard water                          | (c) 61 – 120 ppm hardness                      |
|    | (iv) Very hard water                      | (d) 0 – 60 ppm hardness                        |
| 2. | <b>(A) Coagulant</b>                      | <b>(B) Optimum pH range</b>                    |
|    | (i) Alum [ $\text{Al}_2(\text{SO}_4)_3$ ] | (a) 6 – 10                                     |
|    | (ii) $\text{Fe}_2(\text{SO}_4)_3$         | (b) 7 – 9                                      |
| 3. | <b>A</b>                                  | <b>B</b>                                       |
|    | <b>(Boiler pressure)</b>                  | <b>(Thickness of the scale above which use</b> |
|    | <b>(in psi)</b>                           | <b>of the boiler would be unsafe) (in cm)</b>  |
|    | (i) 475                                   | (a) 0.125                                      |
|    | (ii) 600                                  | (b) 0.19                                       |
|    | (iii) 1800                                | (c) 0.275                                      |



- |    |   |   |
|----|---|---|
| 4. | <b>A</b><br><i>(Nature of feed water)</i> | <b>B</b><br><i>(Suitable phosphate for phosphate treatment)</i> |
|    | (i) Acidic                                | (a) $\text{NaH}_2\text{PO}_4$                                   |
|    | (ii) Correct alkalinity                   | (b) $\text{Na}_2\text{HPO}_4$                                   |
|    | (iii) Alkaline                            | (c) $\text{Na}_3\text{PO}_4$                                    |
- 
- |    |   |   |
|----|---|---|
| 5. | (i) Purest form of natural water<br>(ii) Removal of temporary hardness<br>(iii) Calgon is a trade name of<br>(iv) Brackish water contains<br>(v) Removal of sludges by<br>(vi) 1 mg/l<br>(vii) $1^\circ\text{Fr}$<br>(viii) $M > 2P$<br>(ix) Demineralisation<br>(x) Boiler corrosion | (a) boiling<br>(b) sodium chloride<br>(c) $0.07^\circ\text{C}$<br>(d) sodium hexametaphosphate<br>(e) 10 ppm<br>(f) Ion exchange<br>(g) Carbonates and bicarbonates<br>(h) Mineral Acids<br>(i) Blow-down operation<br>(j) Rain water |
|----|---|---|

### Answers

- |   |                                    |
|---|------------------------------------|
| 1. (i) (d), (ii) (c), (iii) (b), (iv) (a).  | 2. (i) (b), (ii) (a).              |
| 3. (i) (c) ; (ii) (b) ; (iii) (a).  | 4. (i) (c) ; (ii) (b) ; (iii) (a). |
| 5. (i) (j) ; (ii) (a) ; (iii) (d) ; (iv) (b) ; (v) (i) ; (vi) (c) ; (vii) (e) ; (viii) (g) ; (ix) (f) ; (x) (h) |                                    |

### Numerical Problems

#### Type A : (Based on Hardness of Water)

- A water sample contains 204 mg of  $\text{CaSO}_4$  per liter. Calculate the hardness in terms of  $\text{CaCO}_3$  equivalents.  
(Ans. 150 ppm)
- How many grams of  $\text{FeSO}_4$  dissolved per liter gives 210.5 ppm of hardness ?  
(Ans. 0.31996 g/L)
- A sample of water on analysis was found to contain the following impurities expressed in mg/L :
 

Impurity	$\text{Ca}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2$	$\text{CaSO}_4$	$\text{MgSO}_4$
Quantity	10	8.5	12	14
Mol. Wt.	162	146	136	120

 Calculate the temporary, permanent and total hardness of water in mg/L ?  
(Ans. 11.99, 20.49 and 32.48 mg/L)
- A sample of water is found to contain 40.5 mg/L  $\text{Ca}(\text{HCO}_3)_2$ , 46.5 mg/L  $\text{Mg}(\text{HCO}_3)_2$ , 27.6 mg/L  $\text{MgSO}_4$ , 32.1 mg/L  $\text{CaSO}_4$  and 22.45 mg/L  $\text{CaCl}_2$ . Calculate the total hardness of water.  
(Ans. 124.68 ppm)

5. A sample of water on analysis has been found to contain the following in ppm :  
 $\text{Ca}(\text{HCO}_3)_2 = 10.5$  ;  $\text{Mg}(\text{HCO}_3)_2 = 12.5$  ;  $\text{CaSO}_4 = 7.5$  ;  $\text{CaCl}_2 = 8.2$  ;  $\text{MgSO}_4 = 2.6$ .  
 Calculate the temporary and permanent hardness in degree French.  
 (Ans. 1.504 and 1.507 degree French)
6. 100 ml of water sample has a hardness equivalent to 12.5 ml of 0.08 N  $\text{MgSO}_4$ . What is the hardness in ppm ?  
 (Ans. 500 ppm)

### Type B : (Based on Hardness determination by EDTA method)

- 0.28 g of  $\text{CaCO}_3$  was dissolved in HCl and the solution was made to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of the hard water sample required 33 ml of the same EDTA solution on titration. After boiling 100 ml of this water, Cooling, Filtering and then titration required 10 ml of EDTA solution. Calculate the temporary and permanent hardness of water.  
 (Ans. Hardness ; Total = 330, Perm. = 100, Temp. = 230 ppm)
- A standard hard water contains 15 g of  $\text{CaCO}_3$  per liter. 20 ml. Of this required 25 ml. Of EDTA solution. 100 ml. Of sample water required 18 ml. EDTA solution. The same sample after boiling required 12 ml. EDTA solution. Calculate the temporary hardness of the given sample of water, in terms of ppm. (Ans. Temporary hardness = 720 ppm)
- 50 ml of standard hard water containing 1 mg of pure  $\text{CaCO}_3$  per ml consumed 20 ml of EDTA. 50 ml of a water sample consumed 25 ml of the same EDTA solution. Using eriochrome T as indicator, calculate the total hardness of water sample in ppm.  
 (Ans. 1250 ppm)
- Calculate the hardness of a water sample, whose 10 ml required 20 ml of EDTA. 20 ml of  $\text{CaCl}_2$  solution, whose strength is equivalent 1.5 g of  $\text{CaCO}_3$  per litre, required 30 ml of EDTA solution.  
 (Ans. 2000 ppm)
- One gm of  $\text{CaCO}_3$  was dissolved in dil. HCl and the solution diluted to one litre. 50 ml of this solution required 45 ml. of EDTA solution, while 50 ml of the sample water required 18 ml of EDTA solution. On the other hand, 50 ml of boiled sample water when titrated against EDTA consumed 9 ml of solution. Calculate each type of hardness in ppm.  
 (Ans. Perm = 200 ppm ; Temperature = 200 ppm)

### Type C : (Based on Alkalinity of water)

- 200 ml. of a sample of water required 20 ml. of N/50  $\text{H}_2\text{SO}_4$  using methyl orange as indicator but did not give any colouration with phenolphthalein. What type of alkalinity is present ? Express the same in mg/L.  
 (Ans.  $\text{HCO}_3^- = 100$  ppm)
- 200 ml of a sample required 20 ml of N/50 HCl using methyl orange as indicator. Another 200 ml of the same sample required 8 ml of N/50 HCl using phenolphthalein as indicator. Express the alkalinity in terms of mg of  $\text{CaCO}_3$  per litre.  
 (Ans. 80 ppm ( $\text{CO}_3^{2-}$ ) and 20 ppm ( $\text{HCO}_3^-$ ))
- A sample of water was alkaline both to phenolphthalein and methyl orange. 50 ml of this water sample required 15 ml of N/50  $\text{H}_2\text{SO}_4$  for phenolphthalein end point and another 10 ml for complete neutralisation. Calculate the type of alkalinity in ppm.  
 (Ans. 400 ppm ( $\text{CO}_3^{2-}$ ) and 100 ppm  $\text{OH}^-$ )



4. A water sample is not alkaline to phenolphthalein. However, 100 ml of the sample water on titration with N/50 HCl, required 16.9 ml to obtain the end point, using methyl orange as indicator. What are the types and the amounts of alkalinity present in the sample ?  
(Ans.  $\text{HCO}_3^- = 169 \text{ mg/L}$ )
5. A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 ml of water sample on titration with N/50 HCl required 4.7 ml of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and the titration further continued, the yellow colour of the solution just turned red after addition of another 10.5 ml of the acid solution. Elucidate on the type and extent of alkalinity present in the water sample.  
(Ans.  $\text{CO}_3^{2-} = 94 \text{ ppm}$  and  $\text{HCO}_3^- = 58 \text{ ppm}$ )
6. 100 ml of a water sample, on titration with N/50  $\text{H}_2\text{SO}_4$  gave a titre value of 5.8 ml to phenolphthalein end point and another 100 ml. sample on titration with same acid gave a titre value of 11.6 ml to methyl orange end point. Calculate the alkalinity of the water sample in terms of  $\text{CaCO}_3$  and comment on the type of alkalinity present.  
(Ans.  $\text{CO}_3^{2-} = 116 \text{ ppm}$ )
7. 100 ml of water sample, on titration with N/50  $\text{H}_2\text{SO}_4$  using phenolphthalein as indicator, gave the end point when 5 ml of acid were run down. Another lot of 100 ml of the sample also required 5 ml of the acid to obtain methyl-orange end point. What type of alkalinity is present in the sample and what is its magnitude ?  
(Ans.  $\text{OH}^- = 50 \text{ ppm}$ )

#### Type D : (Based on Lime-Soda Process of Water Softening)

1. Calculate the amount of lime and soda required to soften 25,000 litres of water having following analysis :  
 $\text{Ca}(\text{HCO}_3)_2 = 4.86 \text{ ppm}$  ;  $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ ppm}$  ;  $\text{CaSO}_4 = 6.8 \text{ ppm}$  ;  $\text{MgCl}_2 = 5.7 \text{ ppm}$  ;  
 $\text{MgSO}_4 = 9.0 \text{ ppm}$  ;  $\text{SiO}_2 = 3.5 \text{ ppm}$  ;  $\text{NaCl} = 5.85 \text{ ppm}$ .  
 (Ans. L = 490 g ; S = 490 g)
2. Calculate the quantity of lime and soda required for softening 50,000 litres of water containing the following salts per litre :  
 $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg}$  ;  $\text{Mg}(\text{HCO}_3)_2 = 5 \text{ mg}$  ;  $\text{CaSO}_4 = 13.6 \text{ mg}$  ;  $\text{MgSO}_4 = 12.0 \text{ mg}$  ;  
 $\text{MgCl}_2 = 2.0 \text{ mg}$  ; and  $\text{NaCl} = 4.7 \text{ mg}$ .  
 (Ans. L = 1.01 kg ; S = 1.17 kg)
3. Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20,000 litres of water, whose analysis is as follows :  
 $\text{Ca}(\text{HCO}_3)_2 = 40.5 \text{ ppm}$  ;  $\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}$  ;  $\text{MgSO}_4 = 30.0 \text{ ppm}$  ;  
 $\text{CaSO}_4 = 34.0 \text{ ppm}$  ;  $\text{CaCl}_2 = 27.75 \text{ ppm}$  ; and  $\text{NaCl} = 10.00 \text{ ppm}$ .  
 Also calculate the temporary and permanent hardness of water sample.  
 (Ans. L = 1.762 kg ; S = 1.728 kg ; temp. = 50 ppm ; perm. = 75 ppm)
4. Calculate the amounts of lime and soda needed for softening 100,000 litres of water containing  $\text{HCl} = 7.3 \text{ mg/L}$  ;  $\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ mg/L}$  ;  $\text{MgCl}_2 = 9.5 \text{ mg/L}$  ;  
 $\text{NaCl} = 29.25 \text{ mg/L}$  ; (Al = 27 ; Mg = 24 ; Na = 23 ; H = 1 ; Cl = 35.5 ; S = 32 ; O = 16).  
 (Ans. L = 3.7 kg ; S = 5.3 kg)

5. Explain with equations and calculate the quantity of quick lime and soda ash required to soften 10,000 litres of water containing :
- 219 ppm of magnesium bicarbonate and 234 ppm of sodium chloride.
  - 16 ppm of  $\text{Mg}^{2+}$  and 18.3 of  $\text{HCO}_3^-$
  - 1.5 ppm of the free acids, 144 ppm of sulphate ions and 71 ppm of chloride ions.
- (Ans. L = 4.0 kg ; S = 2.226 kg)
6. A water sample, using  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  as a coagulant at the rate of 278 ppm, gave following data on analysis for raw water :
- $\text{Ca}^{2+} = 240$  ppm ;  $\text{Mg}^{2+} = 96$  ppm ;  $\text{CO}_2 = 44$  ppm ;  $\text{HCO}_3^- = 732$  ppm.
- Calculate the lime and soda required to soften 250,000 litres of water.
- (Ans. L = 222 kg ; S = 132.5 kg)
7. Calculate the quantities of lime and soda required for softening 300,000 litres of water, using 20 ppm of sodium aluminate as a coagulant. Impurities in water are as follows :
- $\text{Ca}^{2+} = 160$  ppm ;  $\text{Mg}^{2+} = 96$  ppm ;  $\text{HCO}_3^- = 403$  ppm ; dissolved  $\text{CO}_2 = 34$  ppm.
- (Ans. L = 176.6 kg ; S = 149.4 kg)
8. Calculate the quantities of lime ( $\text{Ca(OH)}_2$ ) and soda (anhyd.  $\text{Na}_2\text{CO}_3$ ) required for cold softening of 125,000 L of water with the following analysis, using 10 ppm of sodium aluminate as coagulant :
- Analysis of raw water :
- $\text{Ca}^{2+} = 95$  ppm ;  $\text{Mg}^{2+} = 36$  ppm ;  $\text{CO}_2 = 66$  ppm ;  $\text{HCO}_3^- = 264$  ppm ;  $\text{H}^+ = 2$  ppm
- Analysis of treated water :  $\text{CO}_3^{2-} = 45$  ppm ;  $\text{OH}^- = 34$  ppm. Write the chemical equations involved.
- (Ans. L = 65.7 kg ; S = 59.1 kg)
9. Calculate the amount of lime and soda required to soften 10,000 litres of water containing the following ions per litre :
- $\text{Mg}^{2+} = 4.8$  mg ;  $\text{Ca}^{2+} = 16.0$  mg ;  $\text{HCO}_3^- = 73.2$  mg.
- (Ans. L = 592 g ; S = Nil)



## ***Fuels and Combustion***

*"There is a sufficiency in the world for man's needs but not for man's greed"*

### **1 INTRODUCTION**

In recent years man's dependence on energy has increased tremendously mainly because of the increase in the standard of living and rapid technological advances. Today energy comes chiefly from the fossil fuels such as petroleum, coal and natural gas. Since these sources of energy will never last forever hence their proper utilization is the main concern these days. In this chapter we will be having the basic understanding of the various fuels available to the mankind. This understanding is necessary also for their proper utilization and conservation for future use.

### **2 DEFINITION AND CLASSIFICATION OF FUELS**

A fuel can be defined as any combustible substance which during combustion gives large amount of industrially and/or domestically useful heat.

#### **Utilization of fuels**

The conversion of potential energy of fuels by combustion into energy in the form of heat is used in the following ways.

- (i) Heat evolved by burning of fuels is used mainly for heating purposes,
- (ii) it can also perform other very important functions like coal, in locomotive engines ; and petrol, in internal combustion engines, are used for doing mechanical work.
- (iii) Coal is also used as a reducing agent in blast furnace.
- (iv) Coal is also used in thermal power plants to generate steam which runs a turbine that generates electrical energy.
- (v) Kerosene, coal, gobar gas and LPG are also used as domestic fuel.
- (vi) Fuels are also used for central heating in houses.

**Classification.** Fuels can be classified :

(A) *On the basis of their occurrence :*

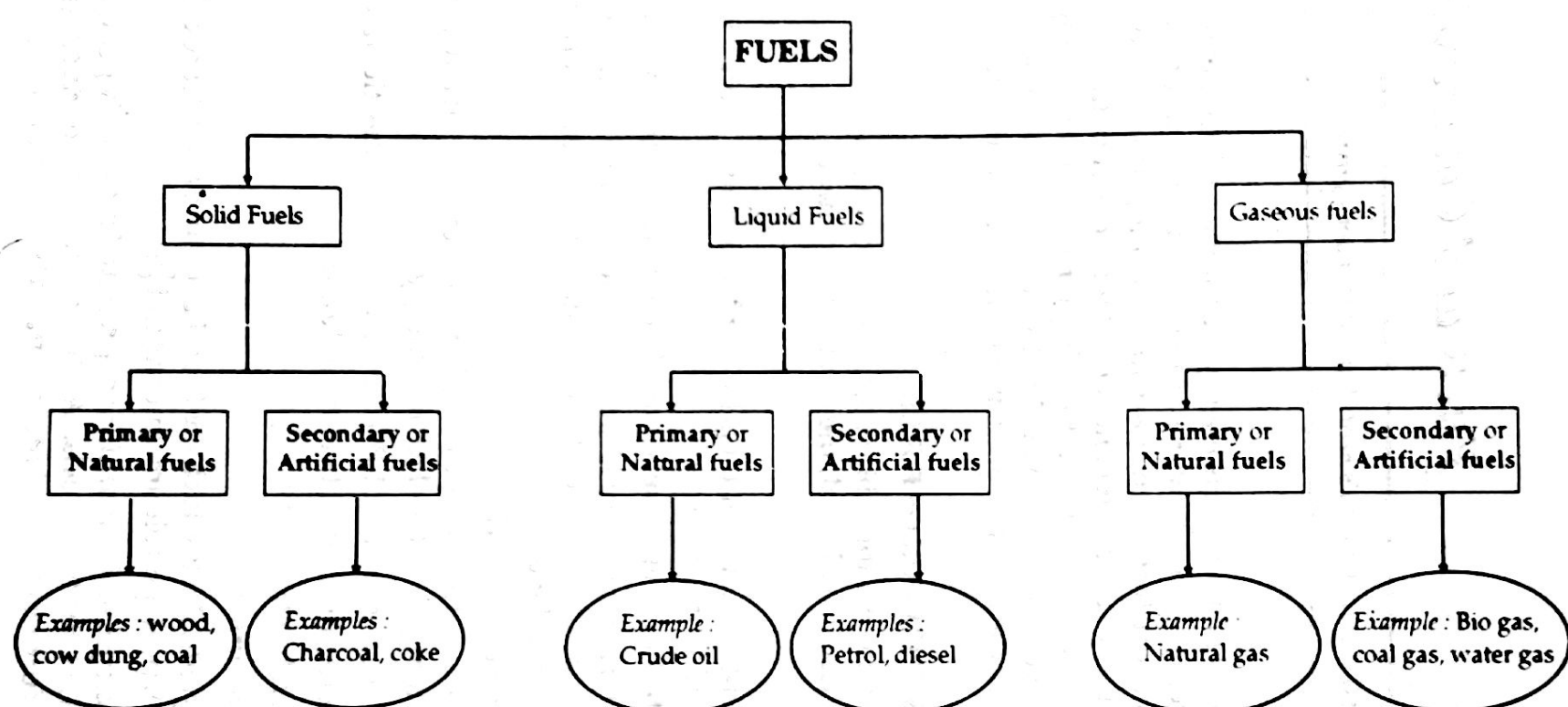
(1) **Natural or primary fuels.** Fuels which are found in nature as such are called natural fuels e.g., wood, coal, peat, petroleum and natural gas.

(2) **Artificial or secondary fuels.** Fuels which are prepared artificially generally from primary fuels are called artificial fuels. As these fuels are derived from naturally occurring fuels by further chemical processing so these are also termed as **secondary fuels**.

Examples of artificial fuels are coke, kerosene oil, petrol, coal gas etc.

(2.1)

The classification of fuels can be summarised as follows :





(B) *On the Basis of physical state of aggregation :*

On this basis, there are three types of fuels viz. solid, liquid and gaseous. The important examples of above categories (A) and (B) of fuels are tabulated below :

**Table 1 : Classifications of Chemical Fuels**

Type of Fuel	Natural or Primary	Artificial or Secondary
Solid	Wood, peat, lignite, Dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum
Gaseous	Natural gas	Coal gas, oil gas, Bio gas, water gas etc.

The primary or main sources of Fuels like coals and petroleum oils are dwindling day-by-day. These are also called 'Fossil Fuels'.

### 3 CHARACTERISTICS OF A GOOD FUEL

1. **High suitability.** A good fuel is one which is most suitable for the desired use. For example, coke made from bituminous coal is most suitable for blast furnace and also as a foundry fuel.

2. **High Calorific value.** Calorific value of a fuel is "The total quantity of heat liberated, from combustion of a unit mass (or volume) of the fuel in air or oxygen. A good fuel should possess high calorific value, since the amount of heat liberated and temperature attained thereby depends upon this property of fuel.

3. **High calorific intensity.** Calorific intensity of a fuel is the maximum temperature attained when fuel is burnt. The calorific intensity of fuel should be high enough to melt the metal

4. **Moderate ignition temperature.** The lowest temperature to which the fuel must be pre-heated so that it starts burning smoothly is called ignition temperature. Low ignition temperature (can cause fire hazards) during storage and transport of fuel, on the other hand, fuel with high ignition temperature is safe for storage, handling and transport but their might be some difficulty during ignition of fuel. Hence, an ideal fuel should have moderate ignition temperature.

5. **Low Moisture content.** The moisture if present in the fuel reduces its heating value. This ultimately leads to loss of money, because moisture is paid for at the same rate as the fuel. Hence, fuel should have low moisture content.

6. **Low non-combustible matter content.** The non-combustible matter remains in the form of ash or clinker, after combustion. It also reduces the heating value. There is additional cost of storage, handling and disposal of the waste involved with it. Hence, a fuel should have low content of non-combustible matter.

7. **Moderate rate of combustion.** If the rate of combustion is low, then a part of the heat liberated may get radiated, instead of raising the temperature hence the required high temperature may not be attained. On the other hand, too high combustion rates are also not required because then it gets out of control. For a continuous supply of heat, fuel must burn with a moderate rate.

8. **Harmless combustion Products.** They should not pollute the atmosphere by emitting CO, SO<sub>2</sub>, H<sub>2</sub>S and other poisonous gases.

9. **Greater flexibility and control.** "Flexibility" means the rate of response in heat liberation with the variation in operating conditions such as fuel or air supply. A fuel which can be easily ignited, which can be burnt at varied rates so that the heat generation is rapid or slow as desired, which can be easily handled, or to sum up, which has a greater flexibility, proves itself to be more preferable and worthy than a fuel which has high calorific value but lower flexibility.

**10. Availability at low cost.** A good fuel is one which is readily and economically available in desired quantity.

**11. Easy to transport.** The transportation of a good fuel is convenient and easy.

**12. Low storage cost.** A good quality fuel is easy to store safely at a low cost.

**13. Controllable combustion** so that combustion can be started or stopped when required.

**14. Uniform size.** In case of solid fuel, the size should be uniform so that combustion is regular.

**15. Efficiency.** A fuel should burn in air with *efficiency* without much smoke.

Relative merits of solid, liquid and gaseous fuels are tabulated below in Table 2.

**Table 2 : Relative Merits of Solid, Liquid and Gaseous Fuels**

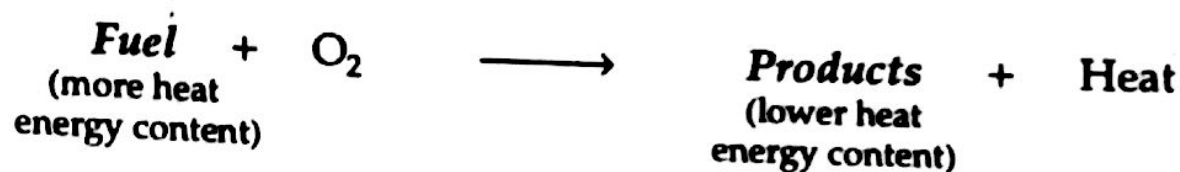
	<b>Fuel Characteristics</b>	<b>Solid Fuels</b>	<b>Liquid Fuels</b>	<b>Gaseous Fuels</b>
1.	Cost	Cheap	More costly than solid fuel	Costly
2.	Storage	Easy	Should be stored in closed containers only.	Must be stored in leak proof voluminous storage tanks.
3.	Risk of fire hazards	Least	Greater	Very high (because these fuels are highly inflammable)
4.	(a) Combustion rate (b) Combustion control	Slow process Not easy	Quick Can be controlled or stopped when needed	Very rapid and efficient. Possible by controlling air supply.
5.	Handling cost	High (Because labour is required in their storage, transport etc.)	Low (Because Liquid and gaseous fuels can be easily transported through pipes)	Low
6.	Ash	Ash is always produced and its disposal is a problem	No ash problem	No ash problem
7.	Smoke	Invariably produced	Burning is clean but high carbon and aromatic liquid fuels may produce smoke.	Smoke is not produced.
8.	Use in Internal combustion engine.	Not possible	Possible	Possible
9.	W/W Calorific value	Least	Higher	Highest
10.	Thermal efficiency	Least	Higher	Highest



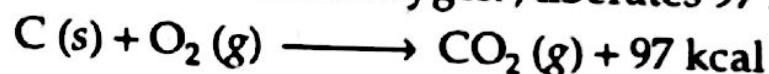
#### 4 COMBUSTION

Combustion is an exothermic chemical reaction. It is accompanied by development of heat and light at a rapid rate, and thus the temperature rises considerably.

During the process of combustion of a fuel (like coal), the atoms of carbon, hydrogen, etc., combine with oxygen with the simultaneous liberation of heat at a rapid rate. This energy is liberated due to the formation of new compounds having less energy (or heat content) in them and therefore, the energy (or heat) released during the combustion process is the difference in the energy of the reactants and that of the product formed.



For example, combustion of carbon in oxygen ; liberates 97 kcal of heat  
i.e.,



*Ignition temperature* is the minimum temperature at which the substance ignites and burns without further addition of heat from outside. The fuel must be preheated to ignition temperature for proper combustion.

#### Conditions for Combustion

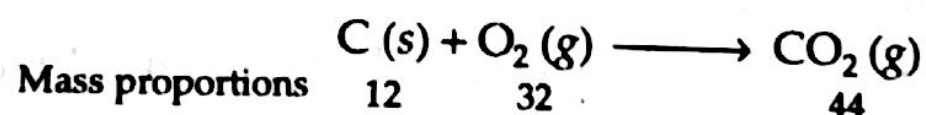
For the combustion of a given fuel, the following conditions must be satisfied :

- (i) Presence of a combustible material,
- (ii) Presence of air (or oxygen) as supporter of combustion,
- (iii) Attainment of ignition temperature.

**Calculation of air quantities.** To find the amount of oxygen and hence, the amount of air required for the combustion of a unit quantity of a fuel, it is necessary to apply the following chemical principles :

(1) "Law of definite proportion". Substances always combine in definite proportions and these proportions are determined by the molecular masses of reactants consumed and the products formed.

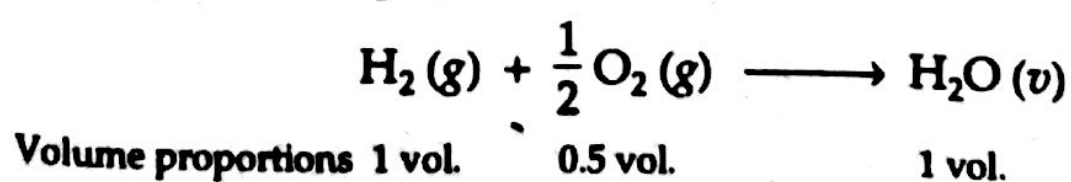
For example,



The above combustion reaction for coke (or carbon) indicates that 12 grams of carbon requires 32 grams of oxygen for complete combustion resulting in the formation of 44 grams of carbon dioxide gas.

In other words, the mass proportions of carbon, oxygen and carbon dioxide are 12 : 32 : 44.

(2) "Law of gaseous volumes" (Gay Lussac 1808). According to this law, "When gases combine, they do so in volumes which bear a simple ratio to each other and also to the product formed provided all gases are measured under similar conditions." For example,



The combustion reaction for hydrogen gas indicates that one volume of hydrogen gas reacts with half volume of oxygen gas to give one volume of water vapour after combustion.

(3) **Avogadro's law.** According to this law, "equal volumes of gases under similar conditions of pressure and temperature possess equal number of moles (or molecules)".

$$V \propto n \quad (\text{at constant } P, T)$$

or  $V \propto N \quad (\text{at constant } P, T)$

where  $n$  and  $N$  are moles or molecules of gases in volume  $V$  at pressure  $P$  and temperature  $T$ .

At 1 atm. pressure and  $0^\circ\text{C}$  temperature, 1 mole of gas contains  $6.023 \times 10^{23}$  molecules of gas.

Moreover, from the corollary of the Avogadro's law, it follows that *one mole of an ideal gas at  $0^\circ\text{C}$  and 1 atm. pressure occupies 22.4 litre volume.*

**Significance of these laws :**

A combustion equation provides a powerful symbolic notation to express qualitative and quantitative details of involved chemical changes.

Consider for example, the combustion reaction for  $\text{CH}_4$ ,

<b>Combustion equation</b>	$\text{CH}_4 (\text{g})$	+	$2\text{O}_2 (\text{g})$	$\longrightarrow$	$\text{CO}_2 (\text{g})$	+	$2\text{H}_2\text{O} (\text{l})$
Weight ratio	16 g		64 g		44 g		36 g
Volume ratio	1 volume		2 volume		1 volume		2 volume
Mole ratio	1 mol		2 mol		1 mol		2 mol
Molecule ratio	$6.023 \times 10^{23}$ molecules		$2 \times 6.023 \times 10^{23}$ molecules		$6.023 \times 10^{23}$ molecules		$2 \times 6.023 \times 10^{23}$ molecules

The combustion reaction suggests that in terms of

- Weight ratio.** 16 g  $\text{CH}_4$  reacts with 64 g  $\text{O}_2$  to form 44 g  $\text{CO}_2$  and 36 g  $\text{H}_2\text{O}$ .
- Volume ratio.** 1 volume  $\text{CH}_4$  reacts with 2 volume  $\text{O}_2$  to form 1 volume  $\text{CO}_2$  and 2 volume  $\text{H}_2\text{O}$ .
- Mole ratio.** 1 mole  $\text{CH}_4$  reacts with 2 moles  $\text{O}_2$  to form 1 mol  $\text{CO}_2$  and 2 moles  $\text{H}_2\text{O}$ .
- Molecule ratio.**  $6.023 \times 10^{23}$  molecules  $\text{CH}_4$  react with  $2 \times 6.023 \times 10^{23}$  molecules of oxygen to form  $6.023 \times 10^{23}$  molecules of  $\text{CO}_2$  and  $2 \times 6.023 \times 10^{23}$  molecules of water.

(4) In actual practice, the combustion is carried out in presence of air. Therefore, from the amount of oxygen required (as calculated on the basis of principles 1 to 3), amount of air is calculated.

(i) Air contains 21 % of oxygen by volume ; and 23 % of oxygen by mass. Hence from the amount of oxygen required by the fuel the amount of air can be calculated. For instance,

$$1 \text{ kg of oxygen is supplied by } \frac{1 \times 100}{23} = 4.35 \text{ kg of air}$$

1 m<sup>3</sup> of oxygen is supplied by  $\frac{1 \times 100}{21} = 4.76$  m<sup>3</sup> of air

(ii) Mean molecular mass of air is taken as 28.94 g mol<sup>-1</sup>.

(iii) Minimum oxygen required for combustion  
= Theoretical oxygen required - O<sub>2</sub> present in the fuel

(iv) Minimum O<sub>2</sub> required should be calculated on the basis of complete combustion. If the combustion products contain CO and O<sub>2</sub>, then excess O<sub>2</sub> is found by subtracting the amount of O<sub>2</sub> required to burn CO to CO<sub>2</sub>.

(5) Non-combustible matters like nitrogen, ash, carbon-dioxide etc. do not require any oxygen for combustion.

(6) The mass of any gas can be converted to its volume at certain temperature and pressure by assuming that the gas behaves ideally and using the gas equation :

$$PV = nRT$$

where  $P$  = Pressure of gas in atmosphere ;

$V$  = volume of gas in litres ;

$N$  = number of moles of the gas

and  $T$  = temperature on Kelvin scale.

**Illustration.** Calculate the weight of CH<sub>4</sub> in a 9 litre cylinder at 16 atm and 27°C ( $R = 0.08$  litre atm K<sup>-1</sup>).

**Solution.** Given  $P = 16$  atm ;  $V = 9$  litre ;  $T = 27^\circ\text{C} = 27 + 273 = 300$  K ;  
 $R = 0.08$  litre atm. K<sup>-1</sup>.

As molar mass of CH<sub>4</sub> =  $12 + 4 \times 1 = 12 + 4 = 16 \Rightarrow M_{\text{CH}_4} = 16$

And

$$PV = nRT$$

$\Rightarrow$

$$PV = \frac{w}{M} RT$$

$\Rightarrow$

$$w = \frac{PV M}{RT}$$

$\Rightarrow$

$$= \frac{16 \times 9 \times 16}{0.08 \times 300} = 90 \text{ g.}$$

(7) The volume of a gas at a given temperature and pressure can be reduced to the corresponding volume at any other specified conditions of temperature and pressure with the help of the following equation (derived from Boyle's law, Charles' law).

$$\boxed{\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}}$$

where  $P_i, V_i, T_i$  are the initial pressure, volume and temperature of the gas and  $P_f, V_f$  and  $T_f$  are final pressure, volume and temperature of the same gas.

**Illustration.** The theoretical quantity of air required for the complete combustion of 1 litre of fuel gas is 2.5 litre under standard temperature and pressure (STP) conditions. Assuming 20% excess air is used, find the volume of air used at 750 mm pressure and 27°C. Assume ideal behaviour.



**Solution.** Air required for combustion of fuel gas at STP = 2.5 litre when 20% excess air is used, then air requirement =  $2.5 \times \frac{120}{100}$

$$\Rightarrow V_i = 3 \text{ litres} \quad \dots(1)$$

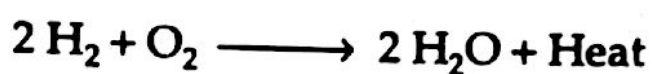
At STP,  $P_i = 760 \text{ mm}$  and  $T_i = 273 \text{ K}$

Moreover, given,  $P_f = 750 \text{ mm}$  and  $T_f = 300 \text{ K}$ ,  $V_f = ?$

As 
$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

$$\Rightarrow V_f = \left( \frac{P_i V_i}{T_i} \right) \times \frac{T_f}{P_f} = \left( \frac{760 \times 3}{273} \right) \times \left( \frac{300}{750} \right) = 3.34 \text{ litres.}$$

(8) The total amount of hydrogen is either present in the combined form (i.e., as  $\text{H}_2\text{O}$ ) or free form. *Combined hydrogen* is a non-combustible substance. Hence it does not take part in combustion. The rest of hydrogen called *available hydrogen* only take part in combustion reaction.



Mass proportions  $\quad \quad \quad 4 \quad \quad 32$

Now 1 part of hydrogen combines chemically with 8 parts by mass of oxygen so the available hydrogen

$$= \left[ \text{Mass of hydrogen} - \left( \frac{\text{Mass of oxygen}}{8} \right) \right]$$

(9) Conversion of volume of air into weight of air or vice-versa

$$\begin{aligned} \text{Density of air } (d_{\text{air}}) &= \frac{\text{Molar mass of air } (M)}{\text{Molar volume of air } (V)} \\ &= \frac{28.94 \text{ g/mol}}{22.4 \text{ L/mol}} \\ &= \frac{28.94}{22.4} \text{ g/L} \end{aligned} \quad \dots(1)$$

Let us assume that for the combustion of a particular fuel,  $m$  gms of air is required.

The corresponding volume of air (let  $v$  litres) requirements can be calculated by assuming that the density of air remains constant (eq. (1) above).

Thus 
$$\frac{m}{v} = \frac{M}{V}$$

$$\boxed{\frac{m}{v} = \frac{28.94}{22.4}} \quad \dots(2)$$

Thus 
$$\boxed{v = \frac{22.4}{28.94} m} \quad \dots(3)$$

(10) Guidelines for combustion calculations :

- (i) Determine the *amounts* of various combustible substances present in a given fuel.
- (ii) Write the *balanced combustion equations* for all the combustible substances present in a given fuel.
- (iii) Calculate the *requirement of oxygen* for complete combustion of fuel constituents either by weight or by volume or by moles.

- (iv) Find the *total oxygen* required by adding up the oxygen requirement for individual combustible substance of the given fuel.
- (v) Calculate *net oxygen* required by subtracting from the total oxygen required, the amount of oxygen already present in the fuel.
- (vi) Convert net oxygen requirement into *total air* requirement.

**Approach : 1. Combustion calculations by weight :**

S.No.	Fuel constituent	Amount of constituent in fuel (gm)	Combustion equation	Weight of oxygen needed for combustion (gm)
1.	C	$a$	$\begin{array}{c} \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \\ 12 \text{ gm} \quad 32 \text{ gm} \end{array}$	$\frac{32}{12} \times a = a'$ *
2.	CO	$b$	$\begin{array}{c} \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \\ (12 + 16) \quad \frac{32}{2} \\ 28 \text{ gm} \quad 16 \text{ gm} \end{array}$	$\frac{16}{28} \times b = b'$
3.	H	$c$	$\begin{array}{c} \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \\ 2 \text{ gm} \quad 16 \text{ gm} \end{array}$	$\frac{16}{2} \times c = c'$
4.	S	$d$	$\begin{array}{c} \text{S} + \text{O}_2 \rightarrow \text{SO}_2 \\ 32 \text{ gm} \quad 32 \text{ gm} \end{array}$	$\frac{32}{32} \times d = d'$
5.	O	$e$	—	—

Total weight of oxygen needed for combustion =  $a' + b' + c' + d' = T$  gms (let)

Weight of oxygen already present in fuel =  $e$  gm

Thus, net weight of oxygen required for combustion =  $T - e = N$  gms (let)

And theoretical weight of air required for combustion =  $N \times \frac{100}{23} = N'$  gms.

**Approach : 2. Combustion calculations by volume :**

S.No.	Fuel constituent	Amount of constituent in fuel ( $\text{m}^3$ )	Combustion equation	Volume of oxygen needed for combustion ( $\text{m}^3$ )
1.	$\text{CH}_4$	$a$	$\begin{array}{c} \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\ 1 \text{ m}^3 \quad 2 \text{ m}^3 \end{array}$	$\frac{2}{1} \times a = a'$ **
2.	$\text{C}_2\text{H}_6$	$b$	$\begin{array}{c} \text{C}_2\text{H}_6 + 3.5 \text{ O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \\ 1 \text{ m}^3 \quad 3.5 \text{ m}^3 \end{array}$	$\frac{3.5}{1} \times b = b'$
3.	$\text{C}_2\text{H}_4$	$c$	$\begin{array}{c} \text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O} \\ 1 \text{ m}^3 \quad 3 \text{ m}^3 \end{array}$	$\frac{3}{1} \times c = c'$

\* Weight of  $\text{O}_2$  needed for combustion of 12 gm of C = 32 gm  
 $\therefore$  Weight of  $\text{O}_2$  needed for combustion of 1 gm of C =  $\frac{32}{12}$  gm  
 $\Rightarrow$  Weight of  $\text{O}_2$  needed for combustion of  $a$  gm of C =  $\frac{32}{12} \times a$

\*\* Volume of  $\text{O}_2$  needed for combustion of 1  $\text{m}^3$  of  $\text{CH}_4$  = 2  $\text{m}^3$   
 $\therefore$  Volume of  $\text{O}_2$  needed for combustion of  $a$   $\text{m}^3$  of =  $\frac{2}{1} \times a$

S.No.	Fuel constituent	Amount of constituent in fuel ( $m^3$ )	Combustion equation	Volume of oxygen needed for combustion ( $m^3$ )
4.	$C_2H_2$	$d$	$C_2H_2 + 2.5 O_2 \rightarrow 2 CO_2 + H_2O$ $1 m^3 \quad 2.5 m^3$	$\frac{2.5}{1} \times d = d'$
5.	$H_2$	$e$	$H_2 + 0.5 O_2 \rightarrow H_2O$ $1 m^3 \quad 0.5 m^3$	$\frac{0.5}{1} \times e = e'$
6.	$CO$	$f$	$CO + 0.5 O_2 \rightarrow CO_2$ $1 m^3 \quad 0.5 m^3$	$\frac{0.5}{1} \times f = f'$
7.	$C_4H_{10}$	$g$	$C_4H_{10} + 6.5 O_2 \rightarrow 4 CO_2 + 5 H_2O$ $1 m^3 \quad 6.5 m^3$	$\frac{6.5}{1} \times g = g'$
8.	$O$	$h$	—	—

Total volume of oxygen needed for combustion

$$= a' + b' + c' + d' + e' + f' + g' = T m^3$$

Volume of oxygen already present in fuel =  $h m^3$

Thus, net volume of oxygen required for combustion =  $(T - h) m^3 = N m^3$

And theoretical volume of air required for combustion =  $N \times \frac{100}{21} = N' m^3$ .

**Approach : 3. Combustion calculations by moles :**

S.No.	Fuel constituent	Amount of constituent in fuel		Combustion equation	Moles of oxygen needed for combustion
		gm	mole		
1.	C	a	$\frac{a}{12} = a'$	$C + O_2 \rightarrow CO_2$ 1 mole 1 mole	$a' \times 1 = a''$
2.	H	b	$\frac{b}{2} = b'$	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ 1 mole 0.5 mole	$b' \times 0.5 = b''$
3.	S	c	$\frac{c}{32} = c'$	$S + O_2 \rightarrow SO_2$ 1 mole 1 mole	$c' \times 1 = c''$
4.	CO	d	$\frac{d}{28} = d'$	$CO + 0.5 O_2 \rightarrow CO_2$ 1 mole 0.5 mole	$d' \times 0.5 = d''$
5.	$CH_4$	e	$\frac{e}{16} = e'$	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$ 1 mole 2 moles	$e' \times 2 = e''$
6.	$C_2H_6$	f	$\frac{f}{30} = f'$	$C_2H_6 + 3.5 O_2 \rightarrow 2 CO_2 + 3 H_2O$ 1 mole 3.5 moles	$f' \times 3.5 = f''$
7.	O	g	$\frac{g}{32} = g'$	—	—

Total moles of oxygen needed for combustion

$$= a'' + b'' + c'' + d'' + e'' + f'' = T \text{ moles (let)}$$

As moles of oxygen already present in fuel =  $g'$  moles

Thus,

net moles of oxygen needed for combustion =  $(T - g') \text{ moles} = N \text{ moles}$



$$\begin{aligned}\text{Weight of oxygen needed for combustion} &= N \text{ moles} \times \frac{32 \text{ gm}}{1 \text{ mole}} \\ &= 32 N \text{ gms} = N' \text{ gm}\end{aligned}$$

$\therefore$  Weight of air required for complete combustion of fuel

$$= N' \times \frac{100}{23} = N'' \text{ gm}$$

Now, volume of air required for complete combustion of fuel

$$= N'' \text{ gm} \times \frac{22.4 \text{ L/mole}}{28.94 \text{ g/mol}} = N'' \times \frac{22.4}{28.94} \text{ L} = N''' \text{ L.}$$

#### 4.1 Solved Examples based on Combustion of Fuel

**Example 1.** Calculate the weight and volume of air required for the combustion of one kg of carbon.

**Solution.**

Constituent	Amount	Combustion equation	Oxygen requirement
C	1000 g	$\begin{array}{ccc} \text{C (s)} + \text{O}_2 \text{ (g)} & \rightarrow & \text{CO}_2 \text{ (g)} \\ 12 \text{ g} & 32 \text{ g} & \\ \text{or } 1 \text{ mol} & 1 \text{ mol} & \\ & (= 22.4 \text{ L}) & \end{array}$	$\frac{32}{12} \times 1000 = 2667 \text{ gm}$ or 22.4 litres

$\therefore$  Theoretical oxygen requirement for the combustion of 1 kg of carbon = 2667 g

Thus, air requirement for complete combustion of 1 kg of carbon

$$= 2667 \times \frac{100}{23} = 11590 \text{ g.}$$

We know that

$$\frac{m}{v} = \frac{M}{V}$$

$$\Rightarrow \frac{11590 \text{ g}}{v} = \frac{28.94 \text{ g mol}^{-1}}{22.4 \text{ L mol}^{-1}}$$

$$\Rightarrow v = \frac{11590 \times 22.4}{28.94} = 8890 \text{ litres.}$$

Thus, volume of air required for complete combustion of 1 kg of carbon = 8890 litres.

#### Alternative method

$$1 \text{ kg C} = 1000 \text{ g carbon} = \frac{1000}{12} \text{ moles of carbon.}$$

As oxygen needed for the combustion of 1 mole of C = 22.4 L

$$\therefore \text{ oxygen needed for the } \frac{1000}{12} \text{ moles of C} = \frac{1000}{12} \times 22.4 \text{ L}$$

$$\Rightarrow \text{ Air requirement} = \left( \frac{1000}{12} \times 22.4 \right) \times \frac{100}{21} = 8890 \text{ litres.}$$

**Example 2.** A gas has the following composition by volume :  $\text{H}_2 = 30\%$  ;  $\text{CH}_4 = 5\%$  ;  $\text{CO} = 20\%$  ;  $\text{CO}_2 = 6\%$  ;  $\text{O}_2 = 5\%$  and  $\text{N}_2 = 34\%$ . If 50% excess air is used find the weight of air actually supplied per  $\text{m}^3$  of this gas. Given molecular weight of air = 28.97.

**Solution.** In one  $\text{m}^3$  of the gas

Fuel Constituents	Composition of constituents	Combustion equation	Volume of $O_2$ needed
$H_2$	(30%) = $0.3 \text{ m}^3$	$  \begin{array}{c}  H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g) \\  1 \text{ m}^3 \quad 0.5 \text{ m}^3  \end{array}  $	$0.3 \times 0.5 = 0.15 \text{ m}^3$
$CH_4$	(5%) = $0.05 \text{ m}^3$	$  \begin{array}{c}  CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \\  1 \text{ m}^3 \quad 2 \text{ m}^3  \end{array}  $	$0.05 \times 2 = 0.1 \text{ m}^3$
$CO$	(20%) = $0.2 \text{ m}^3$	$  \begin{array}{c}  CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g) \\  1 \text{ m}^3 \quad 0.5 \text{ m}^3  \end{array}  $	$0.2 \times 0.5 = 0.1 \text{ m}^3$
			Total = $0.35 \text{ m}^3$
$O_2$	(5%) = $0.05 \text{ m}^3$		Less $O_2$ in fuel gas = $-0.05 \text{ m}^3$
			Net $O_2$ needed = $0.35 - 0.05$ = $0.3 \text{ m}^3 = 300 \text{ L}$

As nitrogen is non-combustible so it does not need oxygen.

Volume of air required for 1 m<sup>3</sup> of gas using 50% excess air

$$= 300 \times \frac{100}{21} \times \frac{150}{100} = 2142.8 \text{ L}$$

Hence, weight of air actually supplied per m<sup>3</sup> of the gas

$$= 2142.8 \text{ L} \times \left( \frac{1 \text{ mol}}{22.4 \text{ L}} \right) \times \left( \frac{28.97 \text{ gm}}{\text{mol}} \right) = 2771 \text{ gm.}$$

**Example 3.** A gaseous fuel has the following composition by volume :

H<sub>2</sub> = 20 % ; CH<sub>4</sub> = 5% ; CO = 20 % ; CO<sub>2</sub> = 5% ; N<sub>2</sub> = 45%.

If 50% excess of air is used, find the weight of air actually supplied per m<sup>3</sup> of this gas.

**Solution.** Volume of components in 1 m<sup>3</sup> of gaseous fuel and O<sub>2</sub> needed for combustion can be calculated as :

Composition	Combustion equation	Volume of O <sub>2</sub> needed
H <sub>2</sub> = 0.20 m <sup>3</sup>	H <sub>2</sub> + 0.5 O <sub>2</sub> → H <sub>2</sub> O	0.20 × 0.5 = 0.1 m <sup>3</sup>
CH <sub>4</sub> = 0.05 m <sup>3</sup>	CH <sub>4</sub> + 2 O <sub>2</sub> → CO <sub>2</sub> + 2 H <sub>2</sub> O	0.05 × 2 = 0.1 m <sup>3</sup>
CO = 0.20 m <sup>3</sup>	CO + 0.5 O <sub>2</sub> → CO <sub>2</sub>	0.2 × 0.5 = 0.1 m <sup>3</sup>
		Total = 0.3 m <sup>3</sup> = 300 L

∴ Volume of air required for 1 m<sup>3</sup> of gas using 50% excess air

$$= 300 \times \frac{100}{21} \times \frac{150}{100} = 2142.8 \text{ L}$$

Hence, weight of air actually supplied per m<sup>3</sup> of gas

$$= \text{volume} \times \frac{28.94}{22.4} = 2142.8 \times \frac{28.94}{22.4} = 2768.4 \text{ L}$$

**Example 4.** Calculate the mass of air needed for complete combustion of 5.0 kg of coal containing 80% carbon, 15% hydrogen and rest oxygen. [Raj. Univ. 1999]

**Solution.** 5 kg coal contains : C = 4000 gms ; H = 750 gms ; and O = 250 gms.

∴ Net weight of oxygen required for combustion

$$= \left[ \frac{32}{12} \times C + \frac{16}{2} \times H \right] - \text{oxygen present in fuel}$$

$$\Rightarrow \text{Net Oxygen} = \left[ \frac{32}{12} \times 4000 + \frac{16}{2} \times 750 \right] - 250 = 16416.7 \text{ gms.}$$

Now, mass of air needed for complete combustion

$$= \text{Net Oxygen} \times \frac{100}{23} = 71376.8 \text{ gms.}$$

$$= 71.38 \text{ kg.}$$



**Example 5.** The percentage composition of coal sample is

$C = 80\%$ ,  $H_2 = 4\%$ ,  $O_2 = 3\%$ ,  $N_2 = 3\%$ ,  $S = 2\%$ ,  $Ash = 5\%$ ,  $Moisture = 3\%$ .

Calculate the quantity of air needed for complete combustion of 1 kg of coal, if 60% excess of air is supplied. [MREC 2001]

**Solution.** 1 kg of coal contains :  $C = 800$  gm,  $H = 40$  gm,  $S = 20$  gm,  $O_2 = 30$  gm.

$$\text{Net } O_2 = \left[ \frac{32}{12} \times 800 + \frac{16}{2} \times 40 + \frac{32}{32} \times 20 \right] - 30 = 2443.3 \text{ gm.}$$

$$\therefore \text{Quantity of air needed} = \text{Net } O_2 \times \frac{100}{23} \times \frac{160}{100} = 16996.9$$

$$= 16.99 \text{ kg.}$$

**Example 6.** A sample of fuel having following percentage composition  $C = 72\%$ ,  $H = 5\%$ ,  $O = 4\%$ ,  $N = 2\%$ ,  $S = 3\%$ ,  $ash = 8\%$  and  $moisture = 6\%$ . Calculate the quantity of air required for the complete combustion of 1 kg of fuel. [MREC 2002]

**Solution.** 1 kg fuel contains :  $C = 720$  gm,  $H = 50$  gm,  $S = 30$  gm,  $O_2 = 40$  gm.

$$\therefore \text{Net } O_2 = \left[ \frac{32}{12} \times 720 + \frac{16}{2} \times 50 + \frac{32}{32} \times 30 \right] - 40 = 2310 \text{ gm.}$$

$$\text{so quantity of air required} = \text{Net } O_2 \times \frac{100}{23} = 10043.5 \text{ gm}$$

$$= 10.04 \text{ kg.}$$

**Example 7.** Calculate the volume of air required for complete combustion of  $1 \text{ m}^3$  of producer gas, whose composition by volume is :  $H_2 = 4.0\%$  ;  $CO = 20\%$  ;  $CH_4 = 8.0\%$  ;  $N_2 = 68\%$ . [RGPV, Dec. 2001]

**Solution.** Volume of components in  $1 \text{ m}^3$  of producer gas and  $O_2$  needed for combustion can be calculated as :

Composition	Combustion equation	Volume of $O_2$ needed
$H_2 = 1 \times \frac{4}{100} = 0.04 \text{ m}^3$	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.04 \times 0.5 = 0.02 \text{ m}^3$
$CO = 1 \times 20/100 = 0.2 \text{ m}^3$	$CO + \frac{1}{2} O_2 \rightarrow CO_2$	$0.2 \times 0.5 = 0.1 \text{ m}^3$
$CH_4 = 1 \times 8/100 = 0.08 \text{ m}^3$	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$	$0.08 \times 2 = 0.16 \text{ m}^3$
		Total = $0.28 \text{ m}^3$

$\therefore$  Volume of air required for complete combustion

$$= 0.28 \times \frac{100}{21} = 1.333 \text{ m}^3.$$

**Example 8.** A gas used in an internal combustion engine had the following composition by volume :  $H_2 = 45\%$ ,  $CH_4 = 36\%$ ,  $CO = 15\%$ ,  $N = 4\%$ . Find the volume of air required for the combustion of  $1 \text{ m}^3$  of the gas. [RGPV, May 2001, Feb. 2005]

**Solution.**

Composition	Combustion equation	Volume of O <sub>2</sub> needed
$H_2 = 1 \times \frac{45}{100} = 0.45 \text{ m}^3$	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.45 \times 0.5 = 0.225 \text{ m}^3$
$CO = 1 \times \frac{15}{100} = 0.15 \text{ m}^3$	$CO + \frac{1}{2} O_2 \rightarrow CO_2$	$0.15 \times 0.5 = 0.075 \text{ m}^3$
$CH_4 = 1 \times \frac{36}{100} = 0.36 \text{ m}^3$	$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$	$0.36 \times 2 = 0.72 \text{ m}^3$
		Total = 1.02 m <sup>3</sup>

$\therefore$  Volume of air required for combustion =  $1.02 \times \frac{100}{21} = 4.857 \text{ m}^3$ .

**Example 9.** Calculate the composition by volume of a mixture of carbon monoxide and methane, 10.5 mL of which required 9 mL of oxygen for its complete combustion.

**Solution.**

Constituent	Amount	Combustion equation	Oxygen requirement
CO	$x \text{ mL (let)}$	$CO + \frac{1}{2} O_2 \rightarrow CO_2$ 1 vol. $\frac{1}{2}$ vol.	$\frac{1}{2} (x) \text{ mL}$
CH <sub>4</sub>	$(10.5 - x) \text{ mL}$	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 vol.    2 vol.	$2 (10.5 - x) \text{ mL}$

$$\text{Total volume of oxygen required} = \left\{ \frac{1}{2} x + 2 (10.5 - x) \right\} \text{ mL} \quad \dots(1)$$

$$\text{Given, volume of oxygen used for combustion} = 9 \text{ mL} \quad \dots(2)$$

From equations (1) and (2),

$$\begin{aligned} \frac{x}{2} + 2 (10.5 - x) &= 9 \\ \Rightarrow x + 4 (10.5 - x) &= 18 \\ \Rightarrow x + 42 - 4x &= 18 \\ \Rightarrow 3x &= 42 - 18 \\ \Rightarrow x &= \frac{24}{3} = 8 \text{ mL} \end{aligned}$$

$\therefore$  Volume of CO = 8 mL.

And volume of CH<sub>4</sub> =  $10.5 - 8 = 2.5 \text{ mL}$ .

## 5 CALORIFIC VALUE

**Calorific value** of a fuel is "the total quantity of heat liberated from the combustion of a unit mass (or unit volume) of the fuel in air or oxygen".

**Units of heat**

1. 'Calorie' is the amount of heat required to increase the temperature of 1 gm of water through one degree centigrade.

2. 'Kilocalorie' (or "kilogram centigrade units") is equal to 1,000 calories. This is the unit of heat in metric system and may be defined as "the quantity of heat required to increase the temperature of one kilogram of water through one degree centigrade. Thus  $1 \text{ kcal} = 1,000 \text{ cal}$ .

3. 'British Thermal Unit'. (B.Th.U.) is defined as "the quantity of heat required to increase the temperature of one pound of water through one degree Fahrenheit. This is the English system unit.

$$1 \text{ B.Th.U.} = 252 \text{ cal} = 0.252 \text{ kcal}$$

or

$$1 \text{ kcal} = 3.968 \text{ B.Th.U.}$$

4. 'Centigrade heat unit'. (C.H.U.) is "the quantity of heat required to raise the temperature of 1 pound of water through one degree centigrade." Thus :  $1 \text{ kcal} = 3.968 \text{ B.Th.U.} = 2.2 \text{ C.H.U.}$

**Higher or gross calorific value (HCV).** Hydrogen is found to be present in almost all fuels and when the calorific value of hydrogen-containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to the room temperature, the latent heat of condensation of steam also gets included in the measured heat, which is then called "higher or gross calorific value."

**Definition of HCV.** The total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled to room temperature.

**Lower or net calorific value.** In actual use of any fuel, the water vapour and moisture, etc. escape as such along with hot combustion gases. Since they are not condensed. Hence, a lesser amount of heat is available. So, *net or lower calorific value* (LCV) is "the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape."

Alternatively, net or lower calorific value (LCV)

$$= \text{HCV} - \text{Latent heat of water vapour formed}$$

Since 1 part by mass of hydrogen produces 9 parts by mass of water.

Hence  $\text{LCV} = \text{HCV} - \text{mass of hydrogen} \times 9 \times \text{Latent heat of steam}$ .

The latent heat of steam is  $587 \text{ kcal/kg}$  or  $1,060 \text{ B.Th.U./lb}$  of water vapour formed at room temperature (i.e.,  $15^\circ \text{C}$ ).

**Units of calorific value**

For solid or liquid fuel : calorie/gram (cal/g) or kilocalorie/kg (kcal/kg) ;

British Thermal unit/lb (B.Th.U./lb)

For Gaseous fuels : kilocalorie/cubic metre ( $\text{kcal/m}^3$ ) ;

B.Th.U./Cubic feet (B.Th.U./ft<sup>3</sup>).

**Relation between various units :**

$$1 \text{ kcal/kg} = 1.8 \times \text{B.Th.U./lb}$$

$$1 \text{ kcal/m}^3 = 0.1077 \times \text{B.Th.U./ft}^3$$

$$1 \text{ B.Th.U./ft}^3 = 9.3 \text{ kcal/m}^3$$



## 6 DETERMINATION OF CALORIFIC VALUE

### 6.1 Bomb Calorimeter

It is an apparatus to measure the heat of combustion or calorific value of solid or non-volatile liquid fuels. This apparatus was devised by Berthelot in 1881.

**Principle.** A known mass of the fuel is burnt and the quantity of heat produced is absorbed in water and measured. The calorific value of the fuel is then determined by applying the principle of calorimetry. That is,

$$\text{Heat liberated mainly from the combustion of fuel} \\ = \text{Heat absorbed by water} + \text{Heat absorbed by apparatus}$$

**Construction.** The bomb calorimeter consists of :

(i) **Bomb.** It is a sealed cylindrical combustion chamber. It is made from stainless steel. It is coated inside with gold or platinum or some other non-oxidisable material to make it corrosion resistant. It is capable of withstanding a pressure of at least 50 atmosphere. The bomb is provided with a air tight lid or cover. The cover can be fitted tightly to the bomb by means of a metal lid screwed down on a lead washer. The lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrodes, a small ring is attached. In this ring, a nickel or stainless steel crucible can be supported.

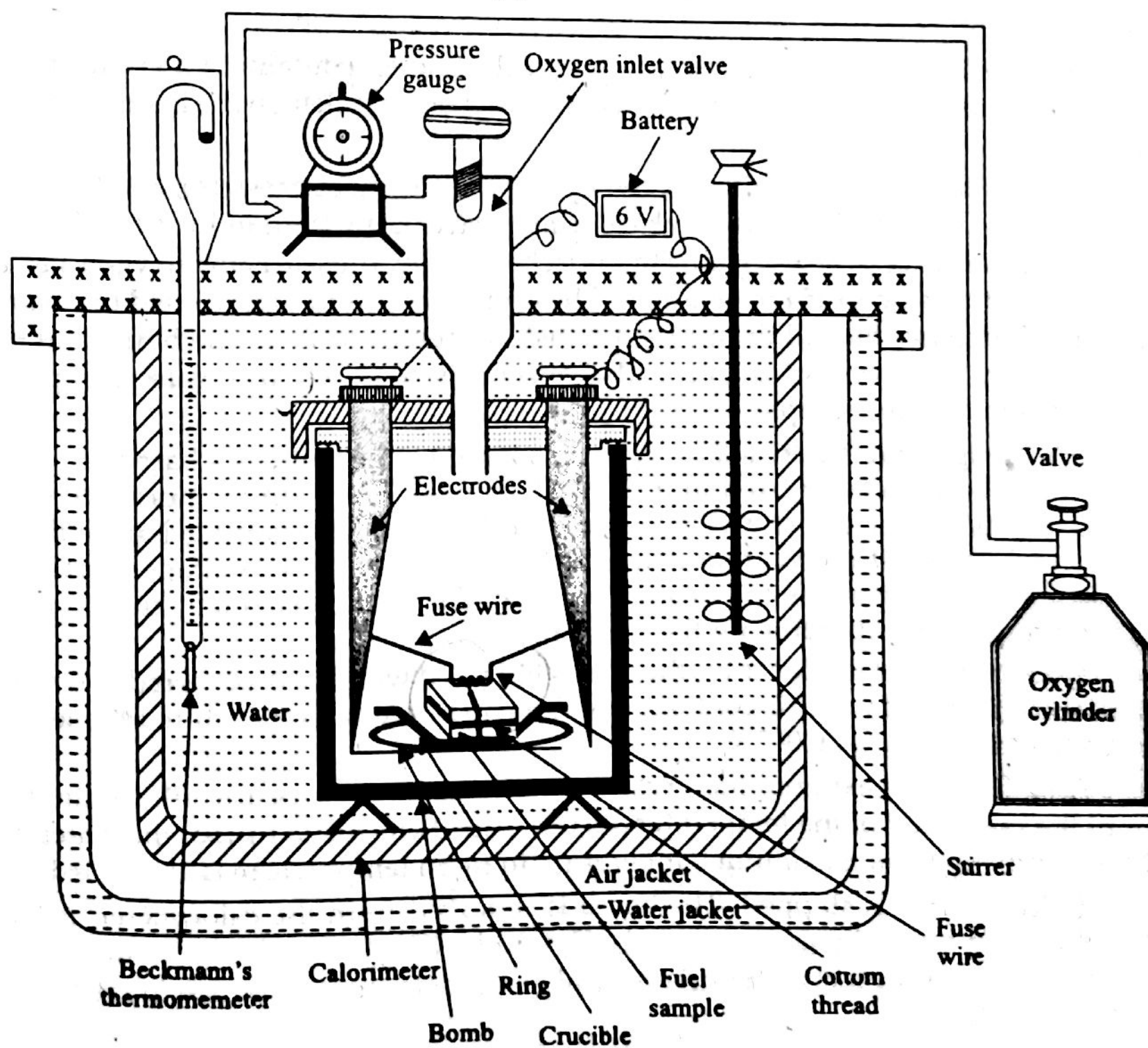


Fig. 1. Bomb Calorimeter.

(ii) **Calorimeter.** It is polished metallic vessel generally made from copper. The bomb is placed inside this copper calorimeter. It also contains a known amount of water sufficient enough so that bomb can be completely submerged.

(iii) **Beckmann's thermometer.** It is an accurate thermometer which can measure temperature upto an accuracy of  $0.01^{\circ}\text{C}$ .

(iv) **Stirrer.** Mostly electrically operated stirrer is used for stirring the water in the calorimeter at a uniform rate.

(v) **Insulated enclosure.** It is double jacketed (air jacket and then water jacket) outer enclosure. Its role is to prevent any loss of heat (due to radiation) to surroundings.

#### **Procedure**

(a) Solid fuel (about 0.5 to 1 gram) is compressed into a pellet. However, if a fuel is non-volatile liquid then it is taken in a capsule. The fuel is then taken in a clean crucible.

(b) A piece of fine platinum wire (0.0075 cm thick) is tightly stretched across the electrodes of the bomb. One end of a piece of a sewing cotton thread is tied round the wire. The crucible is placed in a position, supported over the ring and the loose end of the cotton thread is arranged so as to be in contact with the fuel.

(c) About 10 mL of distilled water is introduced into the bomb to absorb vapours of sulphuric and nitric acids formed during the combustion. The lid of the bomb is tightly screwed.

(d) The bomb is lowered into a copper calorimeter, containing a known mass of water. The calorimeter vessel is then kept in the outer jacket on the insulating feet provided.

(e) The bomb is filled with oxygen upto 25 atmosphere pressure, and then the oxygen inlet valve is closed. A bomb calorimeter works by the combustion of a fuel sample in an excess of oxygen. This is achieved by pressurising oxygen gas a number of times up to 25 atmospheres. These pressurisations are needed to ensure that the bomb has had all the air (and moisture) removed from the bomb and be replaced by an excess of oxygen. The oxygen is required to ensure complete combustion of a fuel sample.

(f) The ignition is initiated by passing a large voltage across a bare fuse wire which has been suitably fixed into the fuel sample. This fixing is normally performed by tying one end of a known mass and length of cotton thread around the fuse and then the other end around the sample (see figure 1). The voltage shorts out the fuse which triggers the combustion reaction. The heat given out by this process is the **energy of combustion** for the substance.

(g) As the fuel sample burns, the heat is liberated which is transferred to water. Uniform stirring of water is continued and the maximum temperature attained is recorded to the nearest  $0.002^{\circ}\text{C}$ .

(h) After the maximum temperature is attained, readings are still continued until the rate of fall of the temperature is uniform. Time taken to cool the water in the calorimeter from maximum temperature to room temperature is also noted.

(i) The stirrer is stopped. The bomb is removed from the calorimeter. After about half an hour, the amounts of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  present in the solution are determined by titration. Sulphuric acid alone is determined by precipitation as barium sulphate.



**Sources of Errors :** The system is prone to errors by either fuse wire breaking or the cotton coming adrift with the increase of gas pressure in pressurisation.

### Observations

Let

- (i) Mass of the fuel taken =  $x$  gm.
- (ii) Mass of water in the calorimeter =  $W$  g.
- (iii) \*Water equivalent of the apparatus =  $\Sigma m.s. = w$  g.
- (iv) Initial temperature of water in the calorimeter =  $T_1$  °C.
- (v) Final temperature of water in the calorimeter =  $T_2$  °C.
- (vi) Higher or gross calorific value of fuel =  $G$  cal/gm.

$$H = m \Delta T$$

*Handwritten note:*  $H = m \Delta T$

### Calculations

$$\text{Heat liberated} = (\text{Mass of fuel}) \times (\text{calorific value of fuel}) = xG \quad \dots(1)$$

$$\begin{aligned} \text{Heat gained by water in calorimeter} &= (\text{mass of water} \times \text{rise in temperature of water} \\ &\quad \times \text{specific heat of water}) \\ &= (W \times (T_2 - T_1) \times 1) \quad \dots(2) \end{aligned}$$

$$\begin{aligned} \text{Heat gained by apparatus} &= (\text{mass of apparatus} \times \text{rise in temperature} \\ &\quad \times \text{specific heat of apparatus}) \\ &= \left\{ \Sigma mS (T_2 - T_1) \right\} = w (T_2 - T_1) \quad \dots(3) \end{aligned}$$

According to the principle of heat exchange in calorimetry :

$$\text{Heat liberated} = \text{Heat gained}$$

$$\begin{aligned} \Rightarrow xG &= W (T_2 - T_1) + w (T_2 - T_1) \\ &= (W + w) (T_2 - T_1) \end{aligned}$$

$$\Rightarrow G = \frac{(W + w) (T_2 - T_1)}{x} \quad \dots(4)$$

### Corrections

The following corrections are applied for getting more accurate results.

(A) The source of heat liberation is not only the combustion of fuel but also the following :

- (i) Heat is also generated by the ignition of fuse wire let  $\Delta H_{FW}$  is the heat liberated due to ignition of fuse wire.

The corresponding correction is known as *fuse wire correction*.

- (ii) As cotton thread is used for igniting the fuel. So, its burning also generates heat.

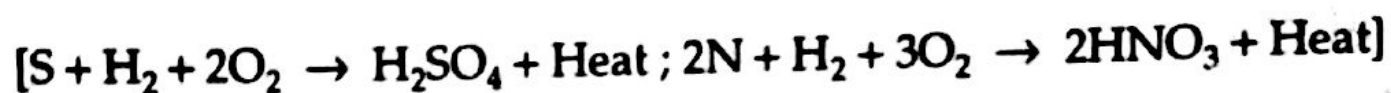
Let  $\Delta H_{CT}$  is the heat liberated due to burning of cotton thread (CT).

$$\text{Moreover, } \Delta H_{CT} = \left( \text{Weight of dry cotton thread used} \right) \times \left( \text{Calorific value of cellulose} = 4140 \text{ Cals/gm} \right)$$

The corresponding correction is known as *cotton thread correction*.



(iii) Under the combustion conditions in bomb calorimeter, sulphur and nitrogen present in fuel are converted into sulphuric and nitric acid respectively.



Formation of both the acids are exothermic reactions. So, the measured heat also includes the heat given out during these acid formations.

Let  $\Delta H_S$  and  $\Delta H_N$  are the heat liberated due to the formation of sulphuric and nitric acid respectively. The corresponding correction is known as *acid correction*.

Using these facts, the correct left hand side for equation (3) becomes :

$$\text{Total heat liberated} = (xG + \Delta H_{FW} + \Delta H_{CT} + \Delta H_S + \Delta H_N) \text{ cal.} \quad \dots(5)$$

(B) For getting accurate value of heat absorption, it is necessary to record correct rise in temperature.

Let (a) initial temperature =  $T_1^\circ\text{C}$

(b) When there is perfect insulation and there is no heat loss, the correct maximum final temperature =  $T_2^c$ .

Although combustion process is very fast, exothermic chain reaction, but it will take some measurable time to observe the final temperature. Suppose,  $T_i$  is the intermediate temperature. Combustion will try to increase the temperature beyond  $T_i$ .

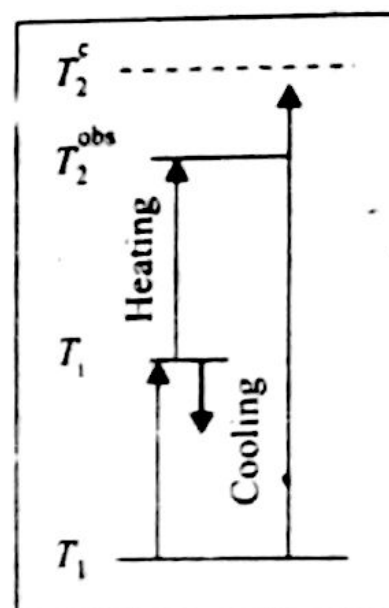


Fig. 2.

However, as  $T_i$  is above room temperature and (practically speaking) some loss of heat occurs due to radiations. Thus, simultaneously cooling will also start. Because of this, the observed maximum temperature ( $T_2^{obs}$  °C) is slightly less than theoretically possible maximum temperature ( $T_2^c$  °C) :

Therefore, it is necessary to get the correct rise in temperature by incorporating cooling correction in the final observed temperature.

For the determination of *cooling correction*, time taken to cool the water in calorimeter from maximum temperature to room temperature (let  $t'$  minutes) is noted, along with fall in temperature at regular intervals of time.

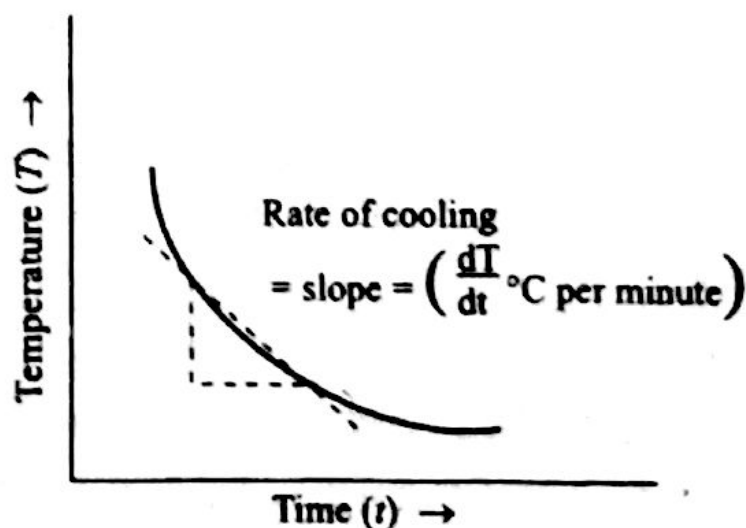


Fig. 3.

A graph is plotted between temperature (along y-axis) and time (along x-axis). The slope of the exponentially decreasing curve gives rate of cooling ( $\frac{dT}{dt}$  °C per minute).

The cooling correction  $\left\{ = \frac{dT}{dt} \times t' (\text{°C}) \right\}$  is then added to the observed rise in temperature.

$$\begin{aligned} \therefore \text{correct maximum final temperature} \\ &= \text{observed maximum final temperature} \\ &\quad + \text{Temperature as per cooling correction} \\ \Rightarrow \quad T_2^c &= T_2^{obs} + T_{cc} \end{aligned} \quad \dots(6)$$

With the help of above result, the correct right hand side in equation (3) becomes :

$$(W + w) (T_2^{obs} + T_{cc} - T_1) \quad \dots(7)$$

Using equations (5) and (7), we have

$$\begin{aligned} (xG + \Delta H_{FW} + \Delta H_{CT} + \Delta H_S + \Delta H_N) &= (W + w) (T_2^{obs} + T_{cc} - T_1) \\ \Rightarrow xG &= \{ (W + w) (T_2^{obs} + T_{cc} - T_1) \} - (\Delta H_{FW} + \Delta H_{CT} + \Delta H_S + \Delta H_N) \\ \Rightarrow G &= \frac{[ \{ (W + w) (T_2^{obs} - T_1 + T_{cc}) \} - (\Delta H_{FW} + \Delta H_{CT} + \Delta H_S + \Delta H_N) ]}{x} \end{aligned}$$

$$\Rightarrow G = \frac{\left[ \begin{array}{c} \{ (W + w) (T_2 - T_1 + \text{cooling correction}) \} \\ - \left\{ \begin{array}{cccc} \text{Fuse} & \text{Cotton} & \text{Sulphuric} & \text{Nitric} \\ \text{wire} & + \text{thread} & + \text{acid} & + \text{acid} \\ \text{correction} & \text{correction} & \text{correction} & \text{correction} \end{array} \right\} \end{array} \right]}{\text{Mass of fuel (= x)}}$$

**Notes :**

**(i) Acid correction guidelines**

- For each mL of N/10  $\text{H}_2\text{SO}_4$  formed, 3.6 calories should be subtracted.
- For each mL of N/10  $\text{HNO}_3$  formed, 1.43 calories should be subtracted.

**(ii) Determination of water equivalent of the apparatus.** Water equivalent of the apparatus is defined as the number of calories required to heat the calorimeter by 1°C.

Let masses of calorimeter, thermometer, stirrer etc. are  $M_C$ ,  $M_T$ ,  $M_{ST}$  etc. And corresponding specific heats are  $S_C$ ,  $S_T$ ,  $S_{ST}$  etc.

$$\begin{aligned} \text{Water equivalent of apparatus} &= M_C S_C + M_T S_T + M_{ST} S_{ST} + \dots \\ &= \Sigma MS. \end{aligned}$$

The water equivalent of the apparatus is best determined by burning a known weight of pure and dry standard fuel like benzoic acid, naphthalene or camphor in the same apparatus under identical conditions as described earlier. The rise in

temperature is noted. The calorific value of standard fuel is known. As all the other values in the formula (eq. 4) are known, the water equivalent of the apparatus can be calculated.

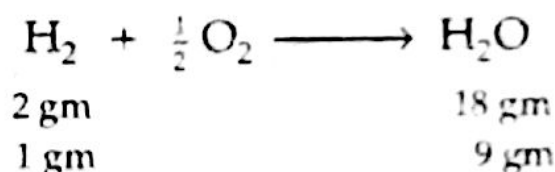
Standard fuel used for water equivalent determination	Gross calorific value (kcal/kg)
1. Benzoic acid	6324
2. Naphthalene	9622
3. Salicylic acid	5269
4. Camphor	9292

(iii) **Determination of Net calorific value.**

Let  $H$  = % of hydrogen in fuel.

Then gms. of hydrogen present in 1 gm fuel =  $1 \times \frac{H}{100}$  gm.

As all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, hydrogen is converted into steam according to



i.e., weight of water produced from 1 gm  $\text{H}_2$  = 9 gm

weight of water produced from  $\frac{H}{100}$  gm  $\text{H}_2$  (or 1 gm fuel) =  $9 \times \frac{H}{100}$  gm  
=  $0.09 H$  gm

Moreover, Latent heat of steam = 587 cal/gm

$\therefore$  Heat taken by water in forming steam (or Latent heat of water vapour formed)  
=  $0.09 H \times 587$  cal

$\therefore$  LCV = HCV - Latent heat of water vapour formed

or

$$\boxed{\text{LCV} = (\text{HCV} - 0.09 H \times 587) \text{ cal/gm.}}$$

## 6.2 Theoretical Calculation of Calorific Value (CV) of a Fuel by Dulong Formula

**Assumption :** CV of a fuel is the sum of the calorific values due to all the components present in the given fuel.

Constituent	C	H	S
GCV	8080	34500	2240

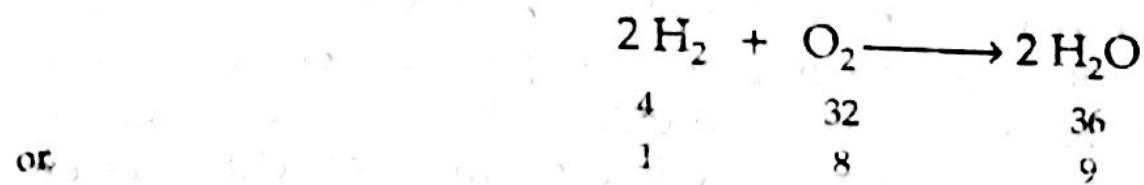
$$\text{Hence, } \boxed{\text{GCV} = \frac{1}{100} \left[ 8080 \%C + 34500 \left( \%H - \frac{\%O}{8} \right) + 2240 \%S \right] \text{ cal/gm}}$$

where,

$\begin{array}{l} \%C = \% \text{ of Carbon} \\ \%H = \% \text{ of hydrogen} \\ \%O = \% \text{ of Oxygen} \\ \%S = \% \text{ of Sulphur} \end{array} \left\{ \begin{array}{l} \text{As determined by the ultimate analysis of the fuels.} \end{array} \right.$



The oxygen, if present in the fuel, is assumed to be, present in the combined form with hydrogen, i.e., in the form of fixed hydrogen ( $H_2O$ ).



i.e., 8 parts of oxygen combine with 1 part of hydrogen to form  $H_2O$ , so

$$\text{Fixed hydrogen} = \frac{\text{Mass of oxygen in the fuel}}{8}$$

Thus, amount of hydrogen available for combustion

$$= \text{Total mass of hydrogen in fuel} - \text{Fixed hydrogen}$$

$$= \left( H - \frac{O}{8} \right)$$

wt. of  $H_2O$  produced from 1 gm  $H_2 = 9$  gm

so, wt. of  $H_2O$  produced from  $\frac{H}{100}$  gm of  $H_2 = 9 \times \frac{H}{100}$  gm =  $0.09 H$  gm

because Latent heat of steam = 587 cal/gm,

so, Latent heat of water vapour formed =  $0.09 H \times 587$  cal.

and  $LCV = HCV - 0.09 H \times 587$  cal/gm.

### 6.3 Determination of Calorific Value by Boy's Gas Calorimeter

It is a standard apparatus used for determining the calorific values of gaseous fuels and those liquid fuels which are easily vaporized.

The Boys Gas Calorimeter was designed by the late Sir Charles Vernon Boys F.R.S. (1855-1944), to provide a simple but accurate method of ascertaining the calorific values of a wide range of gaseous fuel currently in use.

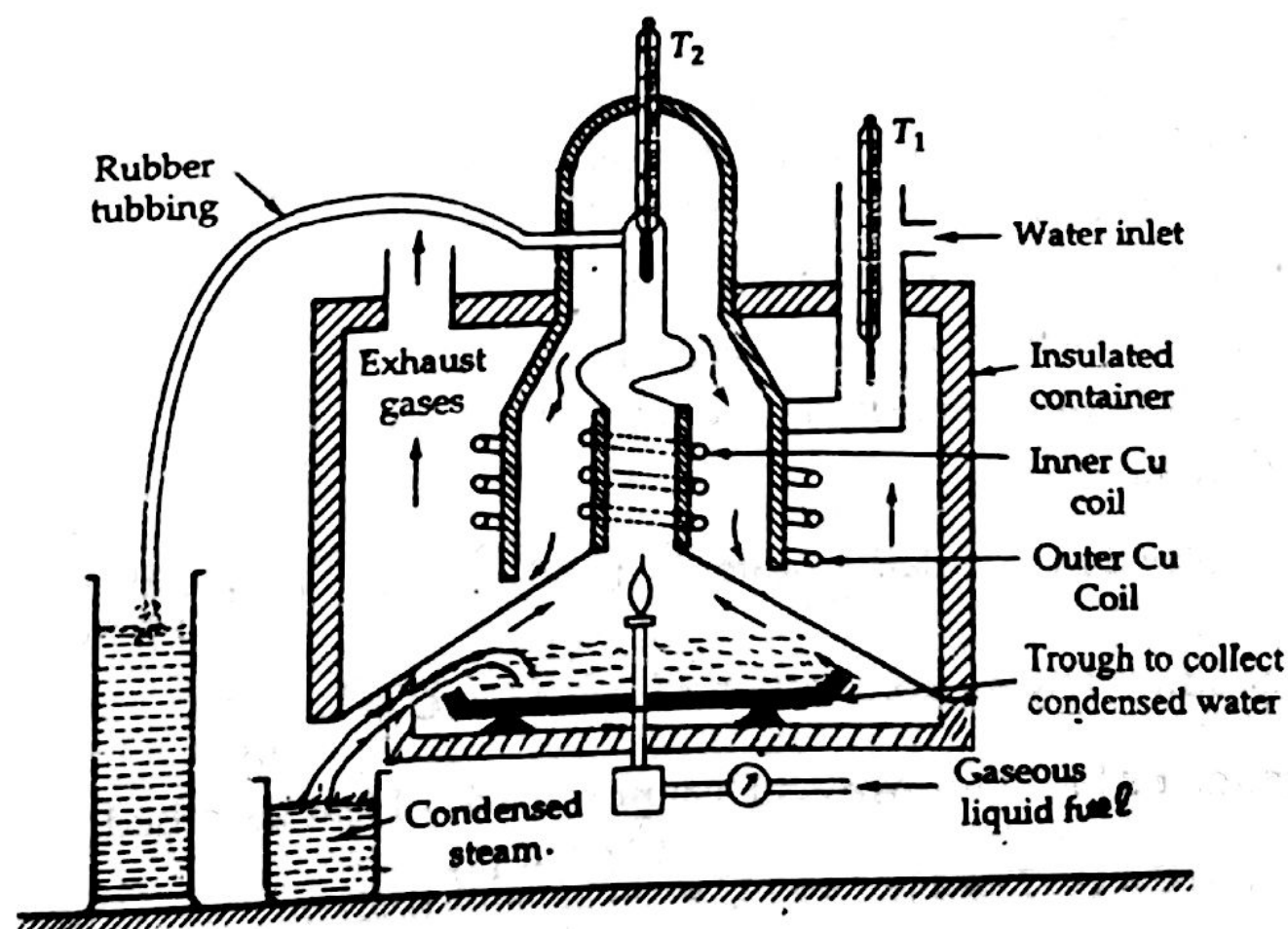


Fig. 4. Boy's gas calorimeter.

**Principle.** The gaseous fuel is burned in a vessel at a constant rate in such a manner that the entire heat is absorbed by water which is circulated in a chimney around the burner. From the volume of the gaseous fuel burnt, the volume of water collected and the rise of temperature of water, the calorific value of the fuel is determined.

**Construction.** The apparatus consists of a suitable gas burner in which a known volume of gas can be burnt at a known pressure and at uniform rate of 3 – 4 litres per minute. Around the burner, there is a combustion chamber or chimney which has a copper tubing coiled inside as well as outside it. Water at a constant rate is passed through the coil. Water enters from the top of the outer coil, moves to the bottom of the chimney and then goes up through the inner coil to the exit at top. The thermometers give the temperatures of the incoming ( $T_1$ ) and outgoing water ( $T_2$ ) respectively. During the process of down and up movement through the coil, the flowing water takes away practically whole of the heat of burner and the steam formed during combustion gets condensed and can be collected as water. The lower portion of chimney is provided with a trough where water condensed from the products of combustion is collected and can be removed through the side tube for measurement of its volume. The whole assembly is enclosed in an insulated chamber.

**Working.** Circulation of water and burning of gaseous fuel are continued at constant rates for about 15 minutes for initial warming up the calorimeter. When the calorimeter gets warmed, the rates of fuel burning and water circulation are adjusted so that the exit water leaves the apparatus nearly at atmospheric pressure. Heat produced by burning of gaseous fuel is transferred to water in the copper coil and the steam formed is condensed back into water which is collected when the steady conditions are established. Then readings are taken simultaneously of :

1. the volume of gaseous fuel burnt at given temperature and pressure in a certain time period ;
2. the quantity of water passing through the coil in the same time ;
3. the steady rise in temperature, i.e., ( $T_2 - T_1$ ). and
4. weight of water condensed during this time.

**Observations :**

Volume of gas burnt at STP in time  $t = V \text{ m}^3$

Weight of water passed through the coil in time  $t = W \text{ kg}$

Temperature of incoming water =  $T_1^\circ \text{C}$

Temperature of outgoing water =  $T_2^\circ \text{C}$

Weight of condensed water (steam) =  $W' \text{ kg}$

Let Higher (gross) calorific value of fuel =  $C \text{ kcal/m}^3$

**Calculations :**

heat absorbed by circulating water =  $W (T_2 - T_1) \times 1 \text{ kg } ^\circ\text{C} \frac{\text{kcal}}{\text{kg } ^\circ\text{C}}$

Heat produced by the combustion of fuel =  $V \times C \text{ m}^3 \times \frac{\text{kcal}}{\text{m}^3}$

Assuming no heat loss, we get Heat produced = Heat absorbed

$$\Rightarrow V \times C = W (T_2 - T_1) \Rightarrow C = \frac{W (T_2 - T_1)}{V} \text{ kcal/m}^3$$

As Latent heat of steam is heat liberated in condensing water vapour and cooling the condensate and is equal to 587 cal/gm or kcal/kg,

Wt. of water condensed from 1 m<sup>3</sup> of gas =  $\frac{W'}{V}$  kg/m<sup>3</sup>

So Latent heat of steam per m<sup>3</sup> of gas =  $587 \text{ kcal/kg} \times \frac{W' \text{ kg}}{V \text{ m}^3} = \frac{W' \times 587}{V} \text{ kcal/m}^3$

∴ Lower calorific value of the fuel = Higher calorific value

$$= C - \frac{W' \times 587}{V}$$

- Latent heat of steam per m<sup>3</sup> of gas

#### 6.4 Determination of Calorific value of Gaseous fuel by Junker's Calorimeter

Junker's calorimeter consists of a vertical cylindrical *combustion chamber* where combustion of gaseous fuel can be carried out with the help of *Bunsen burner*. The supply of gaseous fuel is regulated with the help of *pressure governor*. The volume of gas, flowing in a particular time, is measured with the help of *gasometer*. The combustion chamber is surrounded by an annular water space. Inside the outer flues, heat exchanger coils are also fitted. Radiative and convective heat loss from the calorimeter is prevented with the help of *outer jacket* which is chromium plated. Moreover, the outer jacket contains air which is very good heat insulator. Around the combustion chamber, there is an annular space where water is made to circulate. At the appropriate places there are the openings where *thermometers* are placed for measuring the temperatures of the inlet and outlet water.

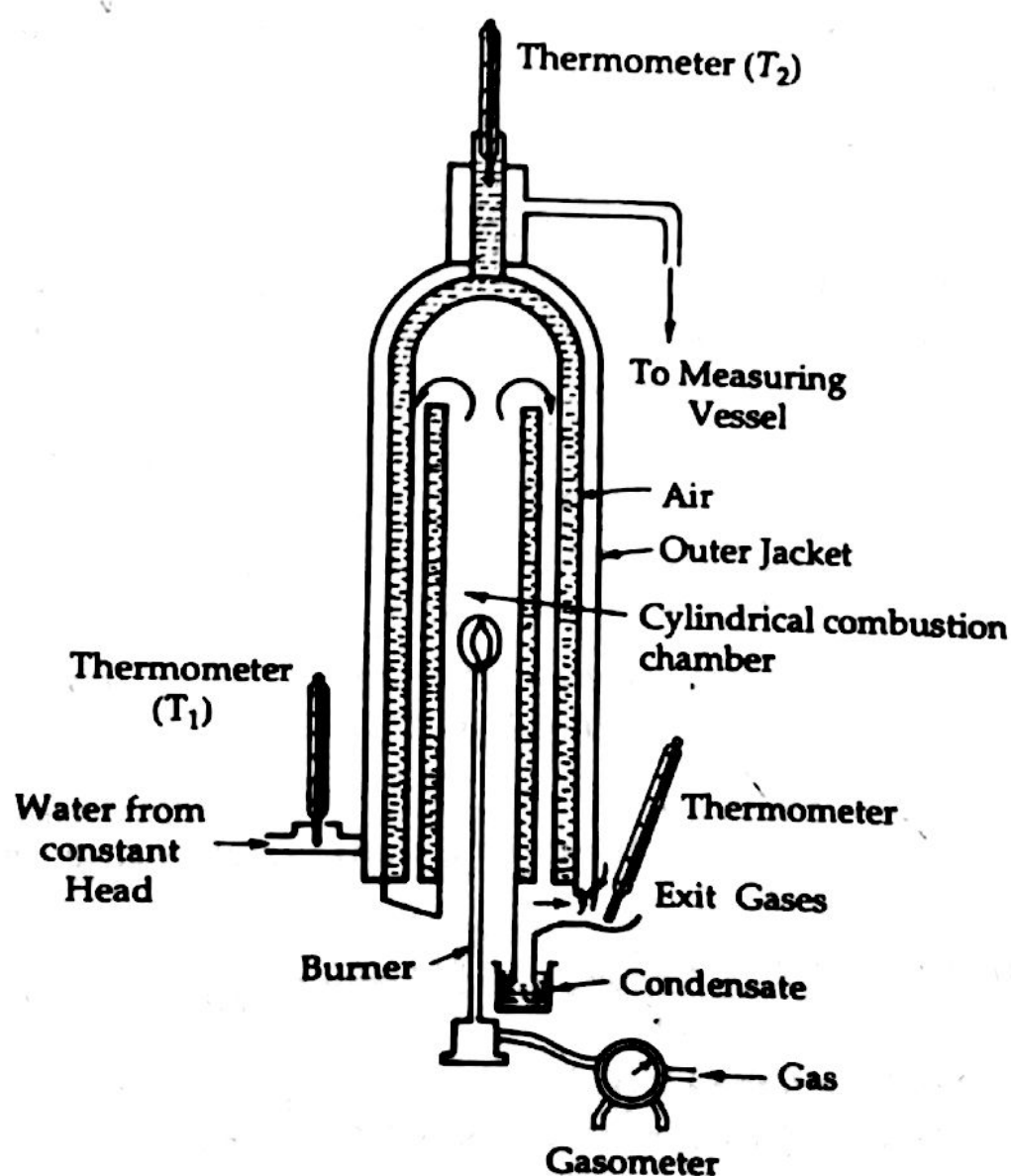


Fig. 5. Junker's gas calorimeter.



A known volume of gas is burned in excess of air at a constant rate in combustion chamber in such a manner that all the heat produced is absorbed in water. Water is flowing at a constant rate in annular space around the combustion chamber. The increase in the temperature of the water is measured and the heat evolved from the burning of the gas can be readily calculated. The weight of water flowing is also recorded for the calculation of calorific value of gaseous fuel.

Let  $V =$  Volume of gas burnt in certain time  $t$  at S.T.P.

$T_1 =$  Temperature of incoming water,

$T_2 =$  Temperature of outgoing water,

$W =$  Weight of water collected in that time  $t$ .

$$\text{Then, Higher Calorific Value (HCV)} = \frac{W(T_2 - T_1)}{V} \text{ kCal/m}^3$$

Now suppose,  $m =$  mass of steam condensed in certain time  $t$  in graduated cylinder from  $V \text{ m}^3$  of gas.

And as Latent heat of steam = 587 kCal/kg.

$$\text{Thus, Lower calorific value (LCV)} = [\text{HCV} - \frac{m}{V} \times 587] \text{ kCal/m}^3$$

### 6.5 Solved Examples based on Calorific Value Determination

**Example 1.** Calculate the gross and net calorific value of a coal sample having the following composition : C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.

$$\begin{aligned} \text{Solution. GCV} &= \frac{1}{100} \left[ 8080\% \text{ C} + 34500 \left( \% \text{H} - \frac{\% \text{O}}{8} \right) + 2240 \% \text{S} \right] \\ &= \frac{1}{100} \left[ 8080 \times 80 + 34500 \left( 7 - \frac{3}{8} \right) + 2240 \times 3.5 \right] = 8828 \text{ kCal/kg.} \end{aligned}$$

$$\begin{aligned} \text{And } \text{NCV} &= \text{GCV} - 0.09\% \text{ H} \times 587 \\ &= 8828 - 0.09 \times 7 \times 587 = 8458 \text{ kCal/kg.} \end{aligned}$$

**Example 2.** A sample of coal containing 89% C : 8% H ; 3% ash. When this coal was tested in the laboratory for its calorific value in the bomb calorimeter, the following data were obtained :

Weight of coal Burnt = 0.85 gm ; Weight of water taken = 650 gm ;

Water equivalent of bomb and calorimeter = 2500 gm ;

Rise in temperature = 2.5 °C ; Cooling correction = 0.03 °C ;

Fuse wire correction = 10 cal ; Acid correction = 50 Cal ;

Assuming that the latent heat of condensation of steam as 580 cal/gm, calculate the (i) gross and (ii) net calorific values of the coal in cal/gm.

**Solution. (i)**

$$\begin{aligned} \text{GCV (or HCV)} &= \frac{(W + w)(T_2 - T_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse correction})}{x} \\ &= \frac{(650 + 2500)(2.5 + 0.03) - (50 + 10)}{0.85} = 9205.2 \text{ cal/gm} \end{aligned}$$

$$\begin{aligned} \text{(ii) NCV (or LCV)} &= \text{HCV} - 0.09 \text{ H} \times 580 \\ &= 9205.2 - 0.09 \times 8 \times 580 = 8787.6 \text{ cal/gm} \end{aligned}$$

**Example 3.** A sample of coal was found to have the following percentage composition by weight : C = 75%, H = 5.2%, O = 12.1%, N = 3.2% and ash = 4.5%.

- (i) Calculate the minimum amount of  $O_2$  and air by weight necessary for complete combustion of 1 kg of coal.  
 (ii) Weight of air required if 40% excess air is supplied.  
 (iii) Gross and net calorific value of coal sample using Dulong's formula.

[Raj. Univ. 2001]

**Solution.** (i) 1 kg of coal contains :

$$C = 750 \text{ gm, } H = 52 \text{ gm, } O = 121 \text{ gm.}$$

$$\begin{aligned} \therefore \text{Net } O_2 &= \left[ \frac{32}{12} \times C + \frac{16}{2} \times H \right] - \text{oxygen present in fuel} \\ &= \left[ \frac{32}{12} \times 750 + \frac{16}{2} \times 52 \right] - 121 = 2295 \text{ gm} = 2.295 \text{ kg} \end{aligned}$$

$$\text{Weight of air required} = 2.295 \times \frac{100}{23} = 9.978 \text{ kg.}$$

(ii) Weight of air required when 40% excess air is supplied

$$= 9.978 \times \frac{140}{100} = 13.97 \text{ kg.}$$

$$\begin{aligned} \text{(iii) GCV} &= \frac{1}{100} [8080 \%C + 34500 (\%H - \%O/8) + 2240 \%S] \\ &= \frac{1}{100} \left[ 8080 \times 75 + 34500 \left( 5.2 - \frac{12.1}{8} \right) + 2240 \times 0 \right] = 7332.2 \text{ kCal/kg.} \end{aligned}$$

$$\begin{aligned} \text{And } \text{NCV} &= \text{GCV} - 0.09 H \times 587 \\ &= 7332.2 - 0.09 \times 5.2 \times 587 = 7057.5 \text{ kCal/kg.} \end{aligned}$$

**Example 4.** The following data is obtained in a bomb calorimeter experiment :

Weight of the fuel sample = 0.95 gm ; Water taken in the calorimeter = 2,400 gm ;  
 Water equivalent of the calorimeter = 600 gm ; Observed rise in temperature =  $2.45^\circ\text{C}$  ;  
 Cooling correction =  $0.055^\circ\text{C}$  ; Acid correction = 65.5 cal ; Fuse wire correction = 3.5 cal ;  
 Cotton thread correction = 1.8 cal. Calculate gross and net calorific values of the fuel sample,  
 if the fuel contains 6.0% H. [RGPV, June 2002]

**Solution.** Gross caloric value (GCV)

$$\begin{aligned} &= \frac{(W + w) (T_2 - T_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse} + \text{cotton thread correction})}{\text{Weight of fuel sample}} \\ &= \frac{[(2400 + 600) (2.45 + 0.055) - (65.5 + 3.5 + 1.8)] \text{ cal}}{0.95 \text{ gm}} \\ &= \frac{7444.2 \text{ cal}}{0.95 \text{ gm}} = 7836 \text{ cal/gm.} \end{aligned}$$

$$\begin{aligned} \text{Net calorific value (NCV)} &= (\text{GCV} - 0.09 H \times 587) \text{ cal/gm} \\ &= 7836 - 0.09 \times 6 \times 587 = 7519.02 \text{ cal/gm.} \end{aligned}$$

**Example 5.** A petrol sample contains 85.0% C, 14% H and 1.0% S. Calculate the minimum air required for complete combustion of 1.0 kg of the petrol sample and its calorific values. [RGPV, Dec. 2002]

**Solution.** One kg of petrol sample contains :

$$C = 1000 \times \frac{85}{100} = 850 \text{ gm ; } H = 1000 \times \frac{14}{100} = 140 \text{ gm ; } S = 1000 \times \frac{1}{100} = 10 \text{ gm}$$

Composition	Combustion reaction	Weight of O <sub>2</sub> needed for combustion
C = 850 gm	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ 12    32	$850 \times \frac{32}{12} = 2266.7 \text{ gm}$
H = 140 gm	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ 2        16	$140 \times \frac{16}{2} = 1120 \text{ gm}$
S = 10 gm	$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$ 32    32	$10 \times \frac{32}{32} = 10 \text{ gm}$
		Total = 2266.7 + 1120 + 10 = 3396.7 gm

∴ Minimum weight of air required for complete combustion of 1 kg of the petrol sample

$$= 3396.7 \times \frac{100}{23} = 14768.3 \text{ kg.}$$

$$\begin{aligned} \text{GCV (or HCV)} &= \frac{1}{100} [8080 \%C + 34500 (\%H - \%O/8) + 2240 \%S] \text{ kcal/kg} \\ &= \frac{1}{100} [8080 \times 85 + 34500 (14 - 0/8) + 2240 \times 1] \\ &= 11720.4 \text{ kcal/kg.} \end{aligned}$$

$$\begin{aligned} \text{NCV (or LCV)} &= [\text{GCV} - 0.09 \text{ H} \times 587] \text{ kcal/kg} \\ &= 11720.4 - 0.09 \times 14 \times 587 = 10,980.8 \text{ kcal/kg.} \end{aligned}$$

**Example 6.** A coal sample has the following % composition

Constituent	C	H	S	N	O	Ash
%	82	3.1	1.1	0.8	3.9	9.1

Calculate the approximate gross calorific value (GCV) and net calorific value (NCV) in cal/gm.

**Solution.** From Dulong's formula :

$$\text{GCV} = \frac{1}{100} \left[ 8080 \%C + 34500 \left( \%H - \frac{\%O}{8} \right) + 2240 \%S \right] \text{ cal/gm.}$$

Here C, H, O and S are the percentage of carbon, hydrogen, oxygen and sulphur respectively.

$$\begin{aligned} \therefore \text{GCV} &= \frac{1}{100} \left[ 8080 \times 82 + 34500 \left( 3.1 - \frac{3.9}{8} \right) + 2240 \times 1.1 \right] \\ &= 7551 \text{ cal/gm} \end{aligned} \quad \dots(i)$$

$$\begin{aligned} \text{Now } \text{NCV} &= [\text{GCV} - 0.09\text{H} \times 587] \text{ cal/gm} \\ &= 7551 - 0.09 \times 3.1 \times 587 = 7387.3 \text{ cal/gm.} \end{aligned}$$

## 7 COAL

Coal is formed from the fossilized remains of animals and plants, hence it is known as *fossil fuel*. Coal and other fossil fuels are used up much more rapidly than it is replenished by nature. Thus it might ultimately result in a fuel shortage. But it has been estimated that coal reserves may last for several hundred years. The factors which are in favour of usage of coals in huge tonnage quantities are : Availability, low cost, least risk of fire hazards and easy storage.



Coal is defined as stratified rock, consisting of organic matter of fuel value, derived from the partial decay and alteration of accumulated plant materials by the action of heat and pressure over million of years. Coal also contains moisture and mineral matter of no fuel value.

### Theories of Coal Formation

The formation of coal is explained by the following two theories

(i) *In-situ theory*. According to it, coal formation took place in the same area where vegetation grew and accumulated. This theory is able to explain the great purity of many coals.

(ii) *Transportation (or drift) theory*. According to this theory, vegetable debris (from vegetation) uprooted and transported from the site of growth by rivers and streams. They were then either deposited in the huge deltas, where rivers run into the sea, or were transported into deep depressions, which got filled and blocked. These huge piles of wood then got buried underground. Under excessive pressure, absence of oxygen, high temperature (greater than  $300^{\circ}\text{C}$ ), presence of bacteria and millions of years of time, the cellulosic material of wood underwent gradual decomposition with the simultaneous liberation of  $\text{CO}_2$  and methane gases. This theory is able to explain the great thickness of coal seams.

The transformation of this vegetable debris to coal takes place in two stages viz. (i) the biochemical or peat stage and (ii) the metamorphic stage.

In fact, the action of decay, pressure and heat convert vegetable and woody remains, deposited many years ago, into coal. The time required for *coalification* is of the order of  $10^7$  and  $10^8$  years.

(i) Coalification is known to take place in two stages : During the first stage of coalification, the cellulosic plant materials are converted into peat by streptococcus, microoccus and various other micro organisms. (This stage is also known as *biochemical coalification* since biological bacterial processes predominate in this stage).

(ii) In the second stage, the agencies responsible for the chemical changes are high temperature ( $> 300^{\circ}\text{C}$ ), pressure and long time of the order of  $10^7 - 10^8$  years. As the effect of these agencies is of varying degrees, the result is coals of different maturity or rank.

Rank is a qualitative measure of carbon content in coal and is defined as the degree or extent of maturation. The soft coals (Peat, lignite and sub-bituminous coals) have low % of carbon contents and are known as low-rank coals. In contrast hard coals (like bituminous and anthracite) have high % of carbon content and are thus classed as high rank.

The formation of coal can also be explained by two alternative theories.

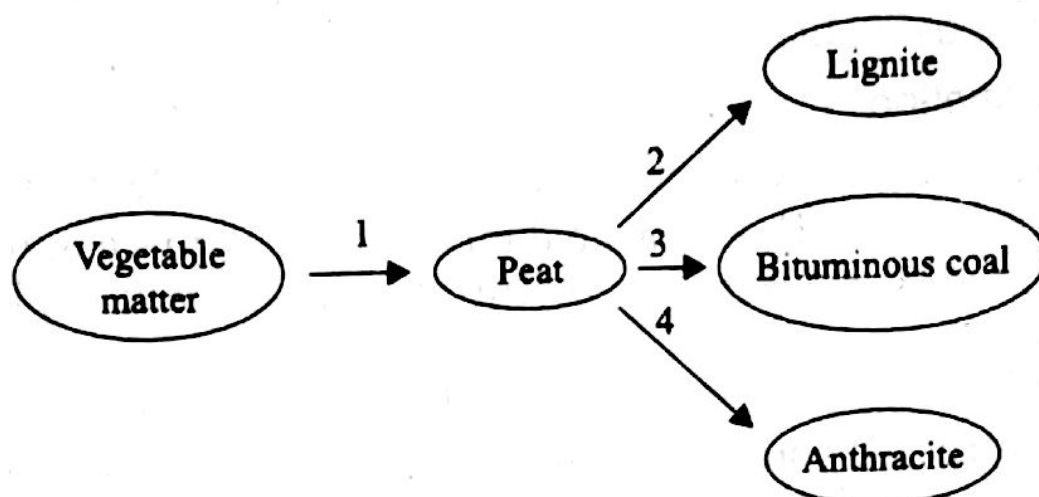
(i) *Serial evolution*. According to this theory, the evolution of coal occurs through geo-chemical metamorphism of peat to anthracite as follows :

Peat  $\rightarrow$  lignite  $\rightarrow$  bituminous coal  $\rightarrow$  anthracite.

This is the commonly accepted theory.

(ii) *Parallel evolution*. According to this theory, the different varieties of coal result from the differences in the extent of the aerobic decomposition of peat, the subsequent composition of the overlying strata and the depth of the burial. Thus, as per this theory, lignites, bituminous coal and anthracite may not form a continuous series.

The parallel evolution theory is based on the concept of entirely biochemical origin of coals of various ranks. This theory may be represented as :

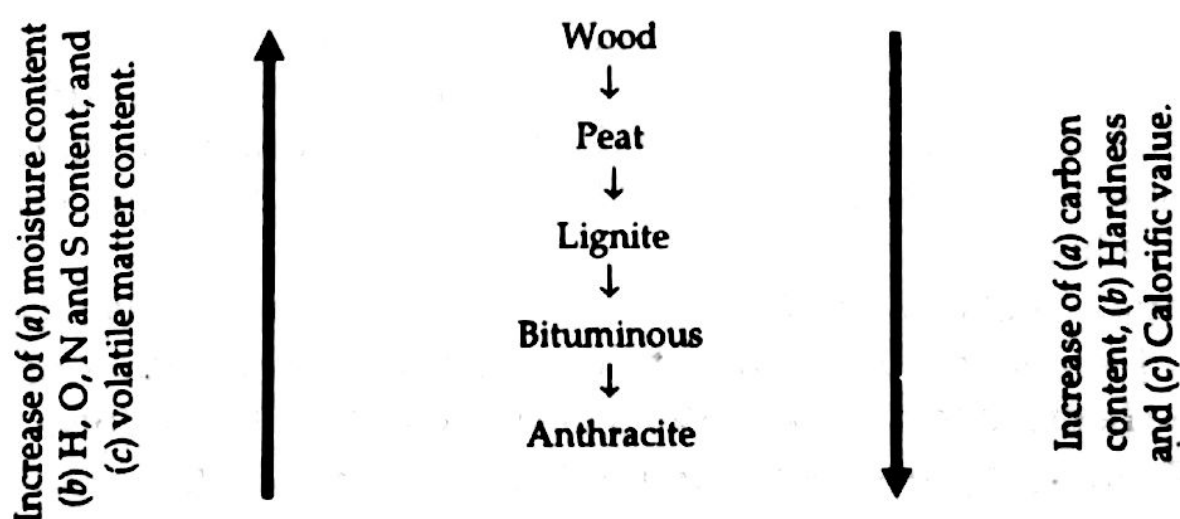


1. *Vegetable matter* undergoes fermentation under the earth and liberate  $H_2$ ,  $CH_4$  and  $CO_2$  with the formation of peat bog. Water causes maceration and certain water soluble compounds get soluble in water resulting in the formation of colloidal solutions like gels and insoluble materials. *Peat* is formed in this stage.

2. Dewatering of raw matter takes place by pressure either in-situ or after transportation to other places. By movement of the earth laminated structures are formed and *peat* is converted into *lignite* under acidic condition or condition of low alkalinity.

3. Under pressure of earth and slowly rising temperature, further dewatering takes place. Due to internal condensation, there occurs formation and loss of  $CO_2$ ,  $CH_4$ ,  $C_2H_6$  and  $H_2O$ . Under this *dynamo chemical or metamorphic stage*, coking constituents from phenolic bodies develop and *bituminous coal* is formed, mainly under conditions of high alkalinity.

4. When the peat stage is prolonged with the continued elimination of  $H_2$  and burial under sedimentary deposits, *Anthracite coal* is formed by alkaline decay under anaerobic condition and loss of  $O_2$  as  $H_2O$  and  $CO_2$ .



The progressive transformation of wood to anthracite can be written as :

It results in increase in carbon content, hardness and calorific value and decrease in volatile matter, moisture and H, O, N and S contents.

The carbon contents, calorific values and main applications of these solid fuels are summarized below in Table 4.

Solid fuel	Percentage (dry, mineral matter free basis)					% Moisture (as found)	Calorific value (kcal/kg)	Main applications
	C	H	O	N	Volatile matter			
Wood	40 – 50	5 – 6	20 – 40	0 – 0.5	—	70 – 90	4000 – 4500	Domestic fuel
Peat	45 – 60	3.5 – 6.8	20 – 45	0.75 – 3	45 – 75	70 – 90	4125 – 5280	Used when there is deficiency of high rank coals.
Lignite (or Brown coal)	60 – 75	4.5 – 5.5	17 – 35	0.75 – 2.1	45 – 60	30 – 50	6600 – 7150	Used for steam generation in thermal power plants and for the production of producer gas.
Bituminous coal	76 – 92	4.0 – 5.6	20 – 30	0.75 – 2	11 – 50	10 – 20	6680 – 8800	Used for steam generation in thermal plants and for domestic heating. It is also used for making coal gas and metallurgical coke.
Anthracite	92 – 95	2.9 – 4.0	2 – 3	0.5 – 2	3.8 – 10	1.5 – 3.5	8470 – 8800	Used in metallurgical purposes where no smoke and high local heat is desired. It is also used in household purposes and steam raising.



## 8 ANALYSIS OF COAL

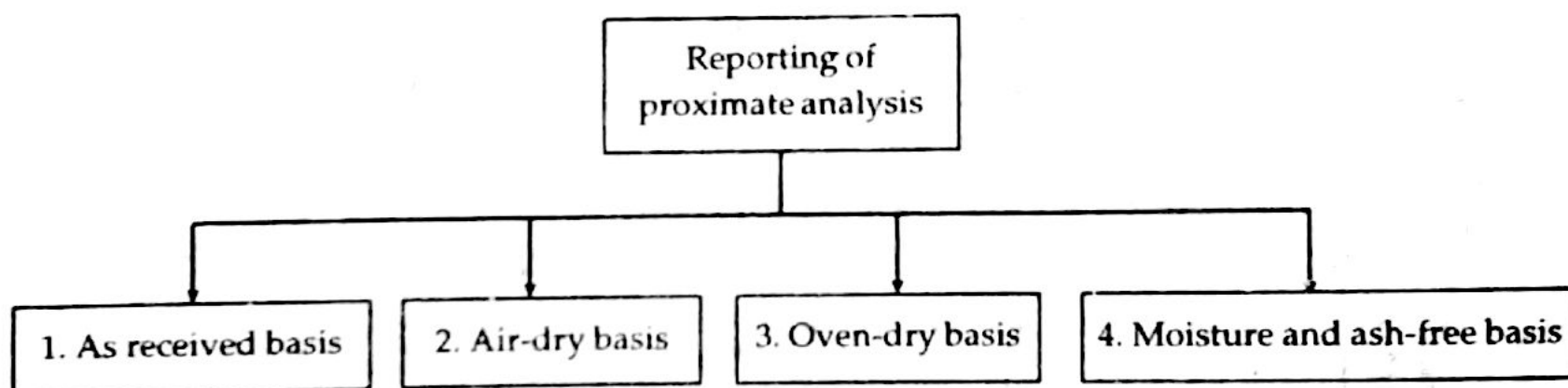
Generally coal is not analyzed by measuring well-defined physico-chemical properties since its composition varies according to the source and age. Mostly consumer-oriented, *empirical tests* are performed for the sake of comparison and for getting some meaningful insights.

In order to ascertain the quality of coal, it is subjected to two types of analysis, viz. proximate and ultimate analysis.

(i) *Proximate analysis*. It is an assay rather than true analysis. This is because the results have no absolute significance. Mostly this assay is carried out in accordance with standard specifications so reproducible results are obtained. The quick and valuable information obtained from the proximate analysis helps in

- (a) Forming opinion regarding cost, quality and probable use of coal in a particular industry,
- (b) classification of coal.

The proximate analysis results can be reported in following ways :



- As received coal may have external (or free or surface) moisture which evaporates on air-drying.
- Air dried coal is free from external moisture but it may still has some internal (or inherent) moisture which is referred to as air-dried moisture. So in proximate analysis on *air-dry basis*, we determine the % of (moisture, volatile matter, ash and fixed carbon).
- *Oven-dry* coal is free from moisture, so proximate results are reported as moisture-free. That means, we analyse coal w.r.t. only volatile matter, ash and fixed carbon.
- *Moisture and ash-free* coal is analysed w.r.t. only volatile matter and fixed carbon in proximate analysis.

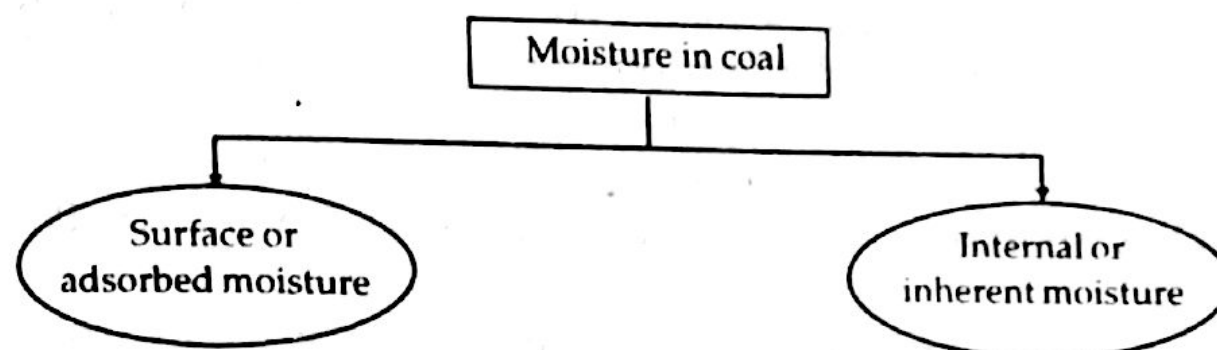
*Proximate analysis* is so called because the data collected vary with the procedure adopted. It gives valuable information about the practical utility of coal. In other words, we can assess the quality of coal by proximate analysis. It includes the determination of Moisture, Volatile matter, Ash and Fixed carbon.

(ii) *Ultimate analysis*. It is useful for combustion calculations. It includes the determination of ultimate constituents present in dry coal like Carbon, Hydrogen, Nitrogen, Sulphur, Ash and Oxygen.

### 8.1 Proximate Analysis

Proximate Analysis involves in the following determinations :

(i) **Moisture Content.** In a coal, moisture may be present as surface or adsorbed moisture, which is lost on air-drying or as inherent moisture that has been retained by an air-dried sample.



In general, coals of high rank contain less of internal moisture. High percentage of moisture is undesirable because :

- (1) It increases the cost of coal as well as its transportation charges.
- (2) It quenches the fire in the furnace. However, presence of moisture upto 10%, produces a more uniform fuel-bed and less of "fly-ash".
- (3) Moisture in coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal.

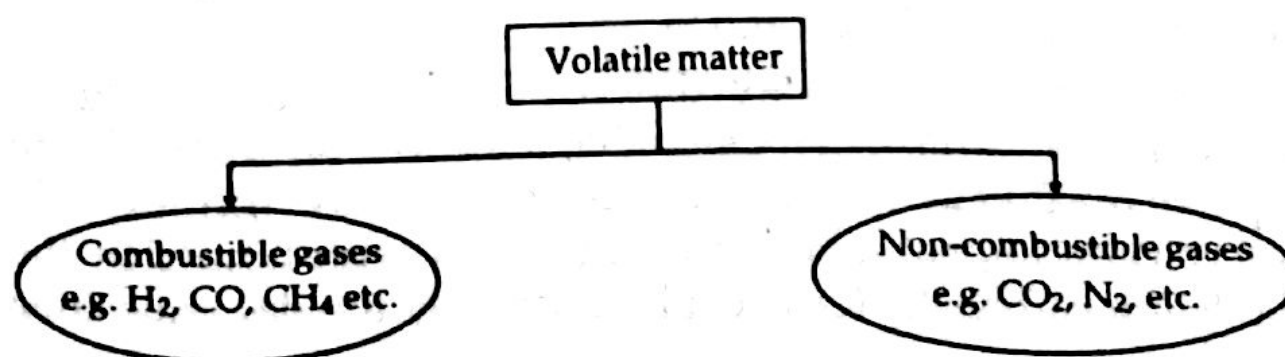
Hence, *lesser the moisture content, better the quality of coal as a fuel.*

**Determination of moisture :** It is the loss of weight of coal when heated at about 105 °C in a crucible.

A known amount of the finely powdered coal sample, taken in a silica crucible, is heated in an electric hot air oven. Heating is done at a temperature of 105° – 110° C for about one hour. After which crucible is taken out with the help of tongs, cooled in a dessicator and weighed. The process of heating, cooling and weighing is repeated till the weight of the crucible containing anhydrous coal becomes constant. Loss in weight is reported as moisture (on percentage basis).

$$\% \text{ of moisture} = \frac{\text{Loss in weight due to removal of moisture}}{\text{wt. of coal taken}} \times 100$$

(ii) **Volatile Matter.** The volatile matter is not a constituent of coal. It consists of a complex mixture of gaseous and liquid products which result from the thermal decomposition of the coal. The extent of decomposition and the yield of volatile matter depends on the conditions of heating particularly the temperature. Thus, it is essential to follow the standard specifications or conditions during the determination of volatile matter.





(1) The volatile matter present in the coal may be combustible gases (such as, hydrogen, CO, methane and other Lower hydrocarbons) or non-combustible gases (like CO<sub>2</sub> and N<sub>2</sub>)

The presence of non-combustible gases is always undesirable, since they do not add to the heat value. Moreover the volume of the furnace required is also large.

(2) When a coal has high volatile matter content then a large proportion of fuel distill over as gas or vapour, a large proportion of which escapes unburnt. So, higher volatile content in coal is undesirable.

(3) A high volatile matter containing coal burns with (i) a long flame, (ii) high smoke and (iii) low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

(4) The volatile matter affects the furnace volume and arrangement of heating space.

A furnace with small combustion volume is not suitable for burning high volatile coals at high rates of combustion. This is because a large proportion of volatile matter will escape unburnt in such circumstances.

(5) In coal gas manufacture and in carbonization plants, volatile matter content is of special significance particularly when by-product recovery is the main object.

High-volatile matter containing coals does not cake well ; where as medium-volatile matter content coals (containing 26-30 % volatile matter) give hard and strong coke on carbonization.

Low volatile matter containing coals does not cake at all and thus unsuitable for coke making.

**Determination of Percentage of volatile matter content.** The moisture free coal is taken in silica crucible and covered with a lid. It is then placed in an muffle furnace, maintained at  $925^{\circ} \pm 20^{\circ} \text{C}$  for 7 minutes. The crucible is then taken out and cooled first in air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage basis.

Thus Volatile matter is the loss in weight of moisture-free coal when heated in a crucible in an muffle furnace at about  $950^{\circ} \text{C}$  for seven minutes.

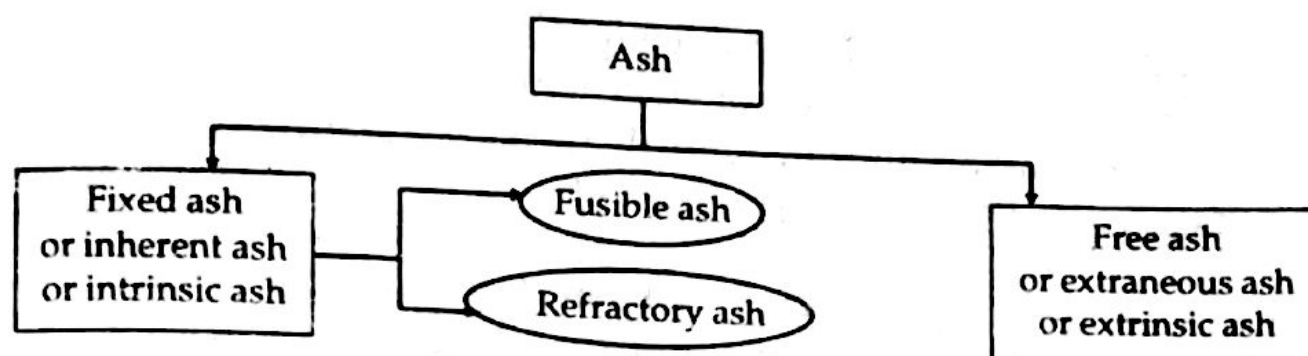
$$\% \text{ of volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{wt. of coal sample taken}} \times 100$$

(iii) **Ash.** Ash is a non-combustible, useless matter which is left behind when all the combustible substances have been burnt off from coal.

The ash which is intimately interspersed within the mass of the coal is called *fixed ash* or *inherent ash* or *intrinsic ash*. It is essentially that mineral matter which was originally present in the vegetable matter from which the coal was formed. It consists of oxides of Na, K, Mg, Ca and Si.

However, the ash which occurs in different layers of the coal is known as *free ash* or *extraneous ash* or *extrinsic ash*. Generally, non-essential mineral matter (usually clay, gypsum or other inorganic materials) give rise to extrinsic ash. It consists of anhydrous calcium sulphate or oxides like calcium oxide formed by the decomposition of calcium carbonate, ferric oxide formed by the decomposition of iron pyrites etc.





The fixed ash content rarely exceeds 1 to 2%, whereas free ash content is relatively high. Fortunately, free ash content can be removed by washing.

Ash is undesirable due to the following reasons :

1. It reduces the calorific value of coal.
2. It causes the hindrance to the flow of air and heat, thereby decreases the efficiency.
3. It also increases transporting, handling and storage costs. There is also additional cost involved in ash disposal.
4. Clinkers (*i.e.*, fused ash lumps) block the interspaces of the grate, on which coal is being burnt. This in turn causes obstruction to air supply. Thereby the burning of coal becomes irregular. Hence, lower the ash content, better the quality of coal.

The fusion temperature of the ash is of particular significance when coal is used in a boiler. Ash with fusion temperature below  $1200^{\circ}\text{C}$  is called *fusible ash* and that above  $1430^{\circ}\text{C}$  is called *refractory ash*.

In general, it has been found that refractory ash contains about 54.2%  $\text{SiO}_2$  and 45.8% alumina, corresponding to the formula  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ .

As the proportion of basic oxides like  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{FeO}$ , etc. increases, the fusion temperature decreases. Thus, fusible ash has higher percentage of basic oxides.

*Do you know that coals used in boilers should have high ash fusion temperatures. This is because of following considerations :*

- (i) When a coal is burnt on grates, fusible ash leads to the formation of lumps of ash (*i.e.*, clinkers) which reduces the primary air supply so the efficiency of production and distribution of heat are adversely affected. Removal of clinkers from grates is laborious and difficult.
- (ii) Some coal particles also get embedded in the fused ash thereby causing loss of fuel.
- (iii) Fused particles of the ash may stick to the boiler tubes and reduce heat transfer.
- (iv) Ash with low melting point forms molten slag which is absorbed in the pores of the refractory lining of the boiler furnace. As the thermal coefficient of expansion and contraction of the ash and refractory material are different so due to spalling, life of the refractory material gets reduced.

**Determination of Ash.** It is the weight of residue obtained after burning a weighed amount of dry coal in an open crucible (*i.e.*, in presence of oxygen or air) at 700 – 750° C for half an hour in a muffle furnace. Heating cooling and weighing is repeated till a constant weight is obtained.

$$\% \text{ of ash} = \frac{\text{wt. of ash formed}}{\text{wt. of dry coal taken}} \times 100$$

(iv) **Fixed Carbon.** Fixed carbon is that hypothetical carbon which burns in the solid state. The fixed carbon content increases from low ranking coals such as lignite to high ranking coals such as anthracite. After the determination of moisture, volatile matter and ash contents, the remaining material is known as fixed carbon.

It also represents the quantity of carbon (in coal) that can be burnt by a primary current of air drawn through the hot bed of a fuel.

The % of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solid state.

Higher the % of fixed C, greater is the calorific value, smaller is % of volatile matter and better the quality of coal.

Hence, high % of fixed C is desirable.

#### Determination of fixed C

It is determined indirectly by deducting the sum total of moisture, ash and volatile matter from 100.

$$\% \text{ of fixed C} = 100 - \% \text{ of (moisture + Volatile matter + ash)}$$

### 8.2 Ultimate Analysis

#### (i) Determination of C and H.

**Importance.** The amount of C, the major combustible constituent of coal depends on the type of coal and its % increases with rank from lignites to anthracites. Thus, % of C forms the basis of classification of coal.

Greater the % of C and H, better is the coal in quality and calorific value.

However, H is mostly associated with the volatile matter and hence, it affects the use to which the coal is put.

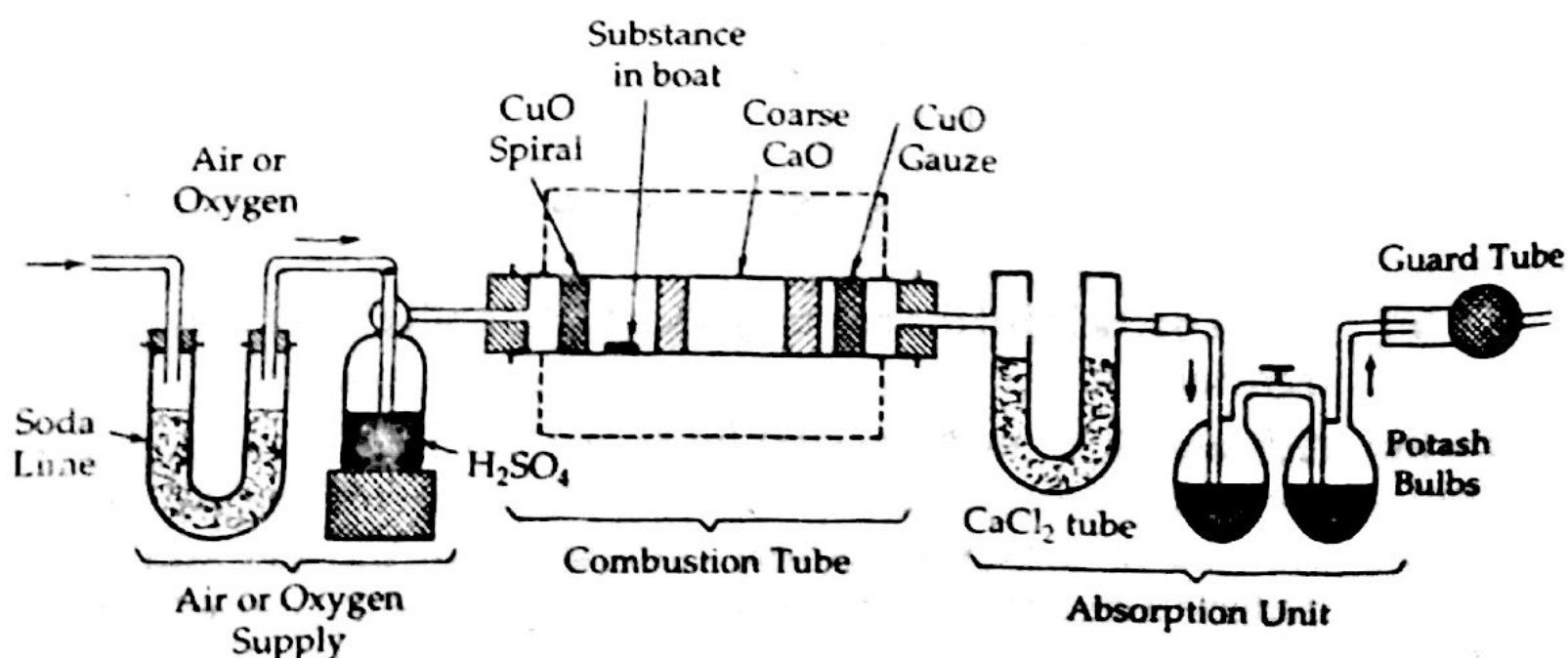
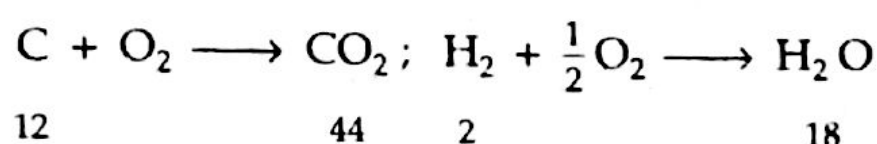


Fig. 5. Carbon and Hydrogen Determination.

**Determination.** A known quantity of coal (About 1-2 gm) is burnt in a current of dry oxygen when C and H present in coal are oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively.

The gaseous products of combustion are passed through two bulbs. One containing weighed amount of anhydrous  $\text{CaCl}_2$  which absorbs water,  $\text{CaCl}_2 + 7\text{H}_2\text{O} \rightarrow \text{CaCl}_2 \cdot 7\text{H}_2\text{O}$  and the other containing weighed amount of  $\text{KOH}$  which absorbs carbon dioxide  $2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$ . The weights of  $\text{CaCl}_2$  and  $\text{KOH}$  in the bulbs are then determined. The increase in the weight of  $\text{CaCl}_2$  bulb represents the weight of water formed, while the increase in the weight of  $\text{KOH}$  bulb represents the weight of  $\text{CO}_2$  formed.



$$\frac{\text{wt. of Carbon (c)}}{\text{wt. of CO}_2 [= \text{Increase in wt. of KOH tube}]} = \frac{\text{Atm. wt. of C (= 12)}}{\text{Mol. wt. of CO}_2 (= 44)}$$

and  $\% \text{ C} = \frac{\text{wt. of C}}{\text{wt. of coal}} \times 100$

$$\therefore \% \text{ of C} = \frac{\text{Increase in wt. of KOH tube} \times 12}{\text{wt. of coal sample taken} \times 44} \times 100$$

Similarly,

$$\frac{\text{wt. of Hydrogen (H}_2\text{)}}{\text{wt. of H}_2\text{O (= Increase in wt. of CaCl}_2\text{ tube)}} = \frac{\text{Mol. wt. of hydrogen (H}_2\text{= 2)}}{\text{Mol. wt. of H}_2\text{O (= 18)}}$$

$$\% \text{ H} = \frac{\text{wt. of Hydrogen}}{\text{wt. of coal}} \times 100$$

$$\therefore \% \text{ of H} = \frac{\text{Increase in wt. of CaCl}_2\text{ tube} \times 2}{\text{wt. of coal sample taken} \times 18} \times 100$$

#### Alternative Derivation

Let, weight of coal sample taken for ultimate analysis =  $w_1$  gm.

Increase in weight of the bulb which contains anhydrous  $\text{CaCl}_2$  =  $w_2$  gm

Increase in weight of the bulb which contains  $\text{KOH}$  =  $w_3$  gm

Thus, weight of water formed after the combustion =  $w_2$  gm

and weight of carbon dioxide formed after the combustion =  $w_3$  gm

We know that,

amount of hydrogen in 18 grams of water = 2 gm

$$\Rightarrow \text{amount of hydrogen in 1 gm of water} = \frac{2}{18} \text{ gm}$$

$$\therefore \text{amount of hydrogen in } w_2 \text{ grams of water} = \frac{2}{18} \times w_2 \text{ gm}$$

$$\text{Thus, amount of hydrogen in } w_1 \text{ gm of coal} = \frac{2}{18} w_2 \text{ gm}$$



$$\Rightarrow \text{Percentage of hydrogen} = \frac{\text{Weight of hydrogen in coal}}{\text{Weight of coal}} \times 100$$

$$= \frac{2 w_2 / 18}{w_1} \times 100$$

$$\Rightarrow \boxed{\% \text{ H} = \frac{2}{18} \times \frac{w_2}{w_1} \times 100}$$

We know that,  
amount of carbon in 44 gms of  $\text{CO}_2 = 12 \text{ gm}$

$$\Rightarrow \text{Amount of C in 1 gm } \text{CO}_2 = \frac{12}{44} \text{ gm}$$

$$\therefore \text{ amount of carbon in } w_3 \text{ grams of } \text{CO}_2 = \frac{12}{44} \times w_3 \text{ gm}$$

$$\text{Thus, amount of carbon in } w_1 \text{ gm of coal} = \frac{12}{44} \times w_3 \text{ gm}$$

$$\text{Now, percentage of carbon} = \frac{\text{Weight of carbon in coal}}{\text{Weight of coal}} \times 100$$

$$= \frac{12 w_3 / 44}{w_1} \times 100$$

$$\Rightarrow \boxed{\% \text{ C} = \frac{12}{44} \times \frac{w_3}{w_1} \times 100}$$

(ii) **Determination of Nitrogen.** Origin of nitrogen in coal is proteins, chlorophyll and alkaloids. Nitrogen is present in heterocyclic linkages in large molecules.

**Importance.** Since nitrogen is an inert and incombustible gas, hence its presence is undesirable. Thus a good quality coal should have very little nitrogen content.

**Determination.** Nitrogen estimation is carried out by Kjeldahl's method.

1. Let  $w_{\text{coal}}$  gm (About 1 gm) of accurately weighed powdered coal is heated with conc.  $\text{H}_2\text{SO}_4$  along with  $\text{K}_2\text{SO}_4$  and  $\text{CuSO}_4$  in a long-necked flask (called Kjeldahl's flask) [Fig. 6(a)].

2. When clear solution is obtained (i.e., when whole nitrogen is converted into ammonium sulphate) it is treated with excess of  $\text{NaOH}$  to liberate ammonia.

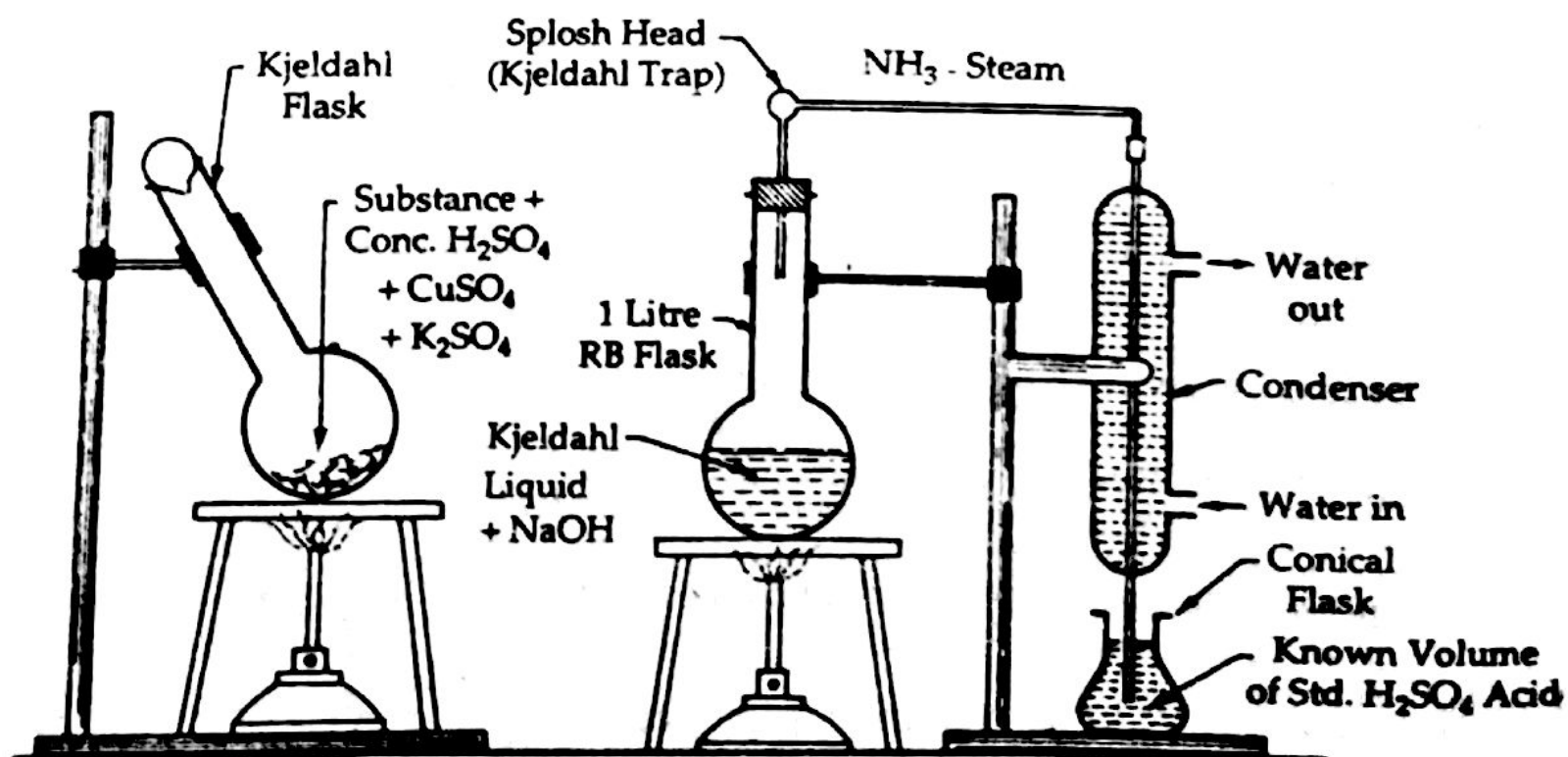
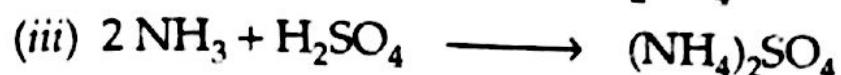
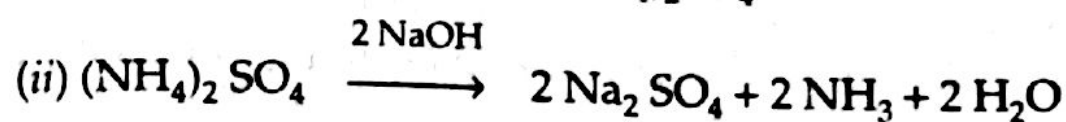
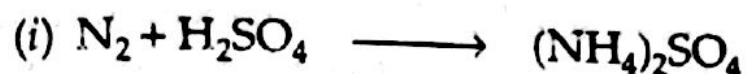


Fig. 6. Estimation of Nitrogen by Kjeldahl's Method.

3. The ammonia thus produced is distilled over and absorbed in a known volume  $V_{H_2SO_4}$  (mL) of standard  $H_2SO_4$  solution of normality  $N_{H_2SO_4}$  [Fig. 6(b)].



4. The volume of unused  $H_2SO_4$  is then determined by titrating against standard NaOH solution of normality  $N_{NaOH}$ . Let  $V_{NaOH}$  (mL) of sodium hydroxide was required to neutralize excess acid.

Thus, the amount of acid neutralized by liberated ammonia (from coal) is determined.

Amount of  $H_2SO_4$  used to neutralize the ammonia evolved

$$= N_{H_2SO_4} V_{H_2SO_4} - N_{NaOH} V_{NaOH} \text{ milli eq.}$$

$$= \frac{N_{H_2SO_4} V_{H_2SO_4} - N_{NaOH} V_{NaOH}}{1000} \text{ equivalents}$$

$$\text{Weight of N} = \frac{N_{H_2SO_4} V_{H_2SO_4} - N_{NaOH} V_{NaOH}}{1000} \times 14$$

$$\% \text{ of N} = \frac{\text{Weight of N}}{\text{Weight of coal sample taken}} \times 100$$

$$= \frac{N_{H_2SO_4} V_{H_2SO_4} - N_{NaOH} V_{NaOH} / 1000}{\omega_{\text{coal}}} \times 14 \times 100$$

$$= \frac{N_{H_2SO_4} V_{H_2SO_4} - N_{NaOH} V_{NaOH}}{\omega_{\text{coal}}} \times 1.4$$

$$\Rightarrow \boxed{\% \text{ of N} = \frac{N_{H_2SO_4} V_{H_2SO_4} - N_{NaOH} V_{NaOH}}{\omega_{\text{coal}}} \times 1.4}$$

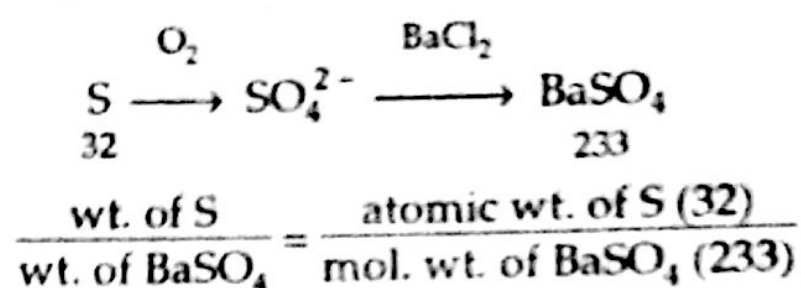
(iii) **Determination of Sulphur.** In coal, sulphur is present as iron pyrites, calcium sulphate or gypsum and as organic sulphur. Sulphur present as iron pyrites can be removed to some extent by washing of coal. Sulphur present as organic sulphur is expelled as  $CS_2$ ,  $H_2S$  and thiophene as a result of carbonisation; but it still remains associated with coke in minute quantities. Sulphur present as  $CaSO_4$  cannot be removed even by the process of carbonisation. Sulphur is an undesirable constituent of coal, and is usually present to the extent of 0.5 to 3%.

**Importance.** Although sulphur increases the calorific value, on oxidation it produces harmful and corrosion causing  $SO_2$  and  $SO_3$  gases. Oxides of sulphur (formed as combustion products) pollute the atmosphere. S is, usually present to the extent of 0.5 to 3% and is derived from ores like iron pyrites, gypsum, etc. mines along-with the coal mines.

Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry, since it is transferred to the iron metal and badly affects the quality and properties of steel.

**Determination.** A known amount of coal is burnt completely in bomb calorimeter in a current of oxygen, by which sulphur present in coal is oxidized to sulphates.

The Ash from the bomb calorimeter is extracted with dil hydrochloric acid. The acid extract is then treated with barium chloride solution to precipitate sulphate as  $\text{BaSO}_4$ . The ppt. of  $\text{BaSO}_4$  is filtered, washed, dried and heated to constant weight.



Let weight of  $\text{BaSO}_4$  precipitate is  $W_2$  gm.

Hence, wt. of S =  $\frac{32}{233} \times W_2$  gm.

Let wt. of coal taken =  $W_1$  gm

% of S in coal =  $\frac{\text{wt. of S}}{\text{Weight of coal}} \times 100$

$\therefore$  % of S in coal =  $\frac{\text{wt. of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{wt. of coal sample taken in Bomb} \times 233}$

$$\Rightarrow \boxed{\% \text{ of S in coal} = \frac{W_2}{W_1} \times \frac{32}{233} \times 100}$$

(iv) **Determination of Ash.** Determination is carried out as in proximate analysis.

(v) **Determination of Oxygen.**

**Importance.** Oxygen is present in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than the actual one.

High oxygen content coals have high inherent moisture and low calorific value.

An increase in 1% oxygen content decreases the calorific value by about 1.7 %.

Thus a good quality coal should have low % of oxygen.

**Determination.** It is determined indirectly by deducting the combined % of (C, H, N, S and ash) from 100.

$$\boxed{\% \text{ of Oxygen} = 100 - \% \text{ of (C + H + N + S + ASH).}}$$

### 8.3 Solved Numerical Examples based on Proximate and Ultimate Analysis

**Example 1.** A sample of coal was analysed as follows :

Exactly 1.5 gm of coal was weighed into a silica crucible. After heating for one hour at  $100^\circ \text{C}$ , the residue weighed 1.415 gm. The crucible was then covered with a vented lid and strongly heated for exactly seven minutes at  $950 \pm 20^\circ \text{C}$ . The residue weighed 0.528 gm. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weight 0.254 gm. Calculate

(i) The percentage results of the above analysis,

(ii) To which type of analysis does the above description below ? Why is the analysis so-named ?



**Solution.** (i) (a) Moisture(%) =  $\frac{\text{loss in weight due to removal of moisture}}{\text{Weight of coal sample taken}} \times 100$   
 $= \frac{1.5 - 1.415}{1.5} \times 100 = 5.67\%$

(b) Volatile matter (%)

$$= \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

$$= \frac{1.415 - 0.528}{1.5} \times 100 = 59\%$$

(c) Ash (%) =  $\frac{\text{Weight of ash left}}{\text{weight of coal taken}} \times 100 = \frac{0.254}{1.5} \times 100 = 16.93\%$

(d) Fixed Carbon (%) =  $100 - \% \text{ of (moisture + volatile matter + ash)}$   
 $= 100 - (5.67 + 59 + 16.93) = 18.4\%$

(ii) This type of analysis is known as proximate analysis because the data collected vary with the procedures adopted.

**Example 2.** 3.12 gm of the coal was Kjeldahlized and  $\text{NH}_3$  gas thus evolved was absorbed in 50 mL of 0.1 N  $\text{H}_2\text{SO}_4$ . After absorption, the excess (residual) acid required 12.5 mL of 0.1 N NaOH for exact neutralization. Determine the percentage of nitrogen in the sample of coal.

**Solution.** Amount of sulphuric acid used to neutralize the ammonia evolved

$$= (0.1 \times 50 - 0.1 \times 12.5) \text{ milli equivalents}$$

$$= \frac{0.1 (50 - 12.5)}{1000} \text{ equivalents}$$

$$\therefore \text{Weight of Nitrogen} = \frac{0.1 (50 - 12.5)}{1000} \times 14$$

$$\text{Percentage of nitrogen} = \frac{\text{Weight of nitrogen}}{\text{Weight of coal sample taken}} \times 100$$

$$= \frac{0.1 (50 - 12.5) \times 14}{1000} \times \frac{1}{3.12} \times 100 = 1.683\%.$$

**Example 3.** 0.1 gm of a sample of coal was used in a bomb calorimeter for the determination of calorific value. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with barium chloride solution and a precipitate of barium sulphate was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was to be 0.01 gm. Calculate the percentage of sulphur in the coal sample.

**Solution.** Percentage of sulphur =  $\frac{\text{weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{weight of coal sample taken in bomb} \times 233}$

$$= \frac{0.01 \times 32 \times 100}{0.1 \times 233} = 1.3734\%$$

**Mini Project #1.** Two samples of coal were analyzed as follows :

Coal sample-1 (S-1)

(i) One gm of accurately weighed coal sample was burnt in a current of oxygen in a combustion apparatus. C and H of the coal were converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$

respectively, which were then absorbed respectively in KOH and  $\text{CaCl}_2$  tubes of known weights. The increase in weight of KOH tube was 2.75 gm and the increase in weight of  $\text{CaCl}_2$  tube was 0.45 gm.

(ii) 1.56 gm of the coal was Kjeldahlized and  $\text{NH}_3$  gas thus evolved was absorbed in 50 mL of 0.1 N  $\text{H}_2\text{SO}_4$ . After absorption, the excess acid required 6.25 mL of 0.1N NaOH for exact neutralization.

(iii) 2.6 gm of the coal sample in a quantitative analysis gave 0.1755 g of  $\text{BaSO}_4$ .

(iv) One gm of an air-dried coal sample was weighed in a silica crucible. The crucible was then heated strongly in oven, until a constant weight was obtained. The last residue was found to weigh 0.1 gm.

*Coal sample-2 (S-2)*

(i) One gm of accurately weighed coal sample was burnt in a current of oxygen in a combustion apparatus. C and H of the coal were converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively, which were then absorbed respectively in KOH and  $\text{CaCl}_2$  tubes of known weights. The increase in weight of KOH tube was 3.08 gm and the increase in weight of  $\text{CaCl}_2$  tube was 0.1167 gm.

(ii) 1 gm of the coal was Kjeldahlized and  $\text{NH}_3$  gas thus evolved was absorbed in 25 mL of 0.1 N  $\text{H}_2\text{SO}_4$ . After absorption, the excess acid required 15 mL of 0.1N NaOH for exact neutralization.

(iii) 0.5 gm of the coal sample a quantitative analysis gave 0.05 g of  $\text{BaSO}_4$ .

(iv) 2.5 gm of an air-dried coal sample was weighed in a silica crucible. The crucible was then heated strongly in oven, until a constant weight was obtained. The last residue was found to weight 0.245 gm.

1. Do the Ultimate analysis for both the coal samples  $S_1$  and  $S_2$ .

2. Find the GCV and NCV ; given latent heat of steam : 587 cal/gm.

3. If  $\text{NCV} > 7200 \text{ cal/gm}$ , then rate of coal is Rs. 950/tonne and coal requirement for 1 unit power generation is 0.7 kg.

If  $\text{NCV} < 7200 \text{ cal/gm}$ , then rate of coal is Rs. 900/tonne and coal requirement for 1 unit power generation is 1 kg.

(a) How much coal will be required (for coal samples  $S_1$  and  $S_2$ ) by a power plant per year for its 1MW power generating unit, if it operates 24 hours daily all the 365 days.

(b) Purchase of which coal sample will be more economical Calculate the savings per year.

(c) Assume you save big amount by the right choice in part (b) and the satisfied boss declares six percent of the total amount per year as incentive. Calculate additional income which you get per month.

4. For installing thermal power plant, Capital cost is Rs. 5 crore per MW. If the plant operates with 34% efficiency, calculate in how many years you can recover the capital cost.

[Given : cost of power generation = Rs. 2/Unit and

Power available to the industry from the public sector is Rs. 5/Unit]

5. After 200 years when all the coal reserves will exhaust, we will not be able to generate electricity in Thermal power plants. Suggest some alternative sources of energy as viable future options.

## Solution. 1. Ultimate Analysis

Constituents (in %)	Formula used	Coal Samples	
		$S_1$	$S_2$
Carbon (C)	$\frac{\text{Increase in wt. of KOH tube}}{\text{Weight of coal sample}} \times \frac{12}{44} \times 100$	$\frac{2.75}{1} \times \frac{12}{44} \times 100 = 75\%$	$\frac{3.08}{1} \times \frac{12}{44} \times 100 = 84\%$
Hydrogen (H)	$\frac{\text{Increase in wt. of CaCl}_2 \text{ tube}}{\text{Weight of coal sample}} \times \frac{2}{18} \times 100$	$\frac{0.45}{1} \times \frac{2}{18} \times 100 = 5\%$	$\frac{0.1167}{1} \times \frac{2}{18} \times 100 = 1.2967\%$
Nitrogen (N)	$\frac{\text{NH}_4\text{SO}_4 \times V_{\text{H}_2\text{SO}_4} - N_{\text{NaOH}} \times V_{\text{NaOH}}}{\text{wt. of coal}} \times 1.4$	$\frac{(50 \times 0.1 - 6.25 \times 0.1)}{1.56} \times 1.4 = 3.926\%$	$\frac{0.1(25 - 15)}{1} \times 1.4 = 1.4\%$
Sulphur (S)	$\frac{\text{Weight of BaSO}_4}{\text{Weight of coal sample}} \times \frac{32}{233} \times 100$	$\frac{0.1755}{2.6} \times \frac{32}{233} \times 100 = 0.927\%$	$\frac{0.05}{0.5} \times \frac{32}{233} \times 100 = 1.37$
Ash	$\frac{\text{Weight of last residue}}{\text{Weight of coal sample}} \times 100$	$\frac{0.1}{1} \times 100 = 10\%$	$\frac{0.245}{2.5} \times 100 = 9.8\%$
Oxygen (O)	$100 - \% \text{ of (C + H + N + S + Ash)}$	$100 - (75 + 5 + 3.926 + 0.927 + 10) = 5.147\%$	$100 - (84 + 1.2967 + 1.4 + 1.37 + 9.8) = 2.134$



## 2. Determination of Gross and Net Calorific Values

Calorific Value	Formula used	Coal Samples	
		$S_1$	$S_2$
Gross (GCV)	$GCV = \frac{1}{100} [8080 C + 34500 (H - 0/8) + 2240 \times S] \text{ cal/gm}$	7583.8 $\frac{\text{cal}}{\text{gm}}$	7173.2 cal/gm
Net (NCV)	$NCV = GCV - 0.09 H \times 587 \text{ cal/r gm}$	7319.65 $\frac{\text{cal}}{\text{gm}}$	7104.7 cal/gm

From the NCV values for  $S_1$  and  $S_2$ , it can be inferred from the data given in 3, that

Coal Sample	$S_1$	$S_2$
Rate of coal	Rs. 950/tonne	Rs. 900/tonne
Coal requirement for 1 unit power generation	0.7 kg	1.0 kg

3. (a) For 1 MW power generating unit, the number of units produced per year will be

$$1 \text{ MW} \times 24 \text{ hrs.} \times 365 = 1000 \text{ kW} \times 24 \text{ hrs} \times 365 \\ = 8760000 \text{ kWhr's or units}$$

Thus, requirement of coal per year for sample

$$S_1 = 8760000 \times 0.7 \text{ kg} \times \frac{1 \text{ Tonne}}{1000 \text{ kg}} \\ = 6132 \text{ tonnes}$$

$$\text{sample } S_2 = 8760000 \times 1 \text{ kg} \times \frac{1 \text{ Tonne}}{1000 \text{ kg}} = 8760 \text{ tonnes}$$

(b) Amount required for purchasing sample 1 for one year

$$= 6132 \text{ tonnes} \times \frac{\text{Rs } 950}{\text{Tonne}} = 5,825,400 \text{ Rs} \quad \dots(i)$$

Similarly, Amount required for purchasing sample 2 for one year

$$= 8760 \times 900 = 78,84,000 \text{ Rs.} \quad \dots(ii)$$

Thus, savings per year for purchasing coal sample  $S_1$

$$= (ii) - (i) = 78,84,000 - 58,25,400 = 20,58,600 \text{ Rs.} \quad \dots(iii)$$

$$(c) \text{ Incentive per year} = (iii) \times \frac{6}{100}$$

$$= 20,58,600 \times \frac{6}{100} = 1,23,516 \text{ Rs.}$$

$$\text{Thus, additional income per month (as incentive)} = \frac{1,23,516}{12} = 10,293 \text{ Rs.}$$

4. Given capital cost = Rs. 5 crores;

From answer 3 (a), above

Installed capacity = 87,60,000 units/year

Given that plant operates with 34% efficiency ; so units of power generated

$$= 87,60,000 \times \frac{34}{100} = 29,78,400 \text{ units/year}$$

$\therefore$  The profit per unit for generation of power

$$= \text{Rs. } 5 - \text{Rs. } 2 = \text{Rs. } 3/\text{unit.}$$

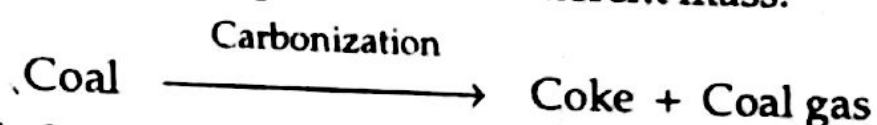
Thus, total profits in one year =  $29,78,400 \times 3 = 89,35,200$  Rs.  
= 89.352 lakhs Rs.

∴ Time required for recovery of capital cost  
=  $\frac{500 \text{ lakhs}}{89.352 \text{ lakhs/year}} = 5.596$  year's

5. Alternative sources of energy for future  
= solar, wind, hydel and nuclear energies.

## 9 CARBONIZATION

The process of converting coal into coke is called *carbonization*. When a coking coal is heated in the absence of air, the porous, hard and strong residue left is called *coke*. Coke is white, lustrous, dense, porous and coherent mass.

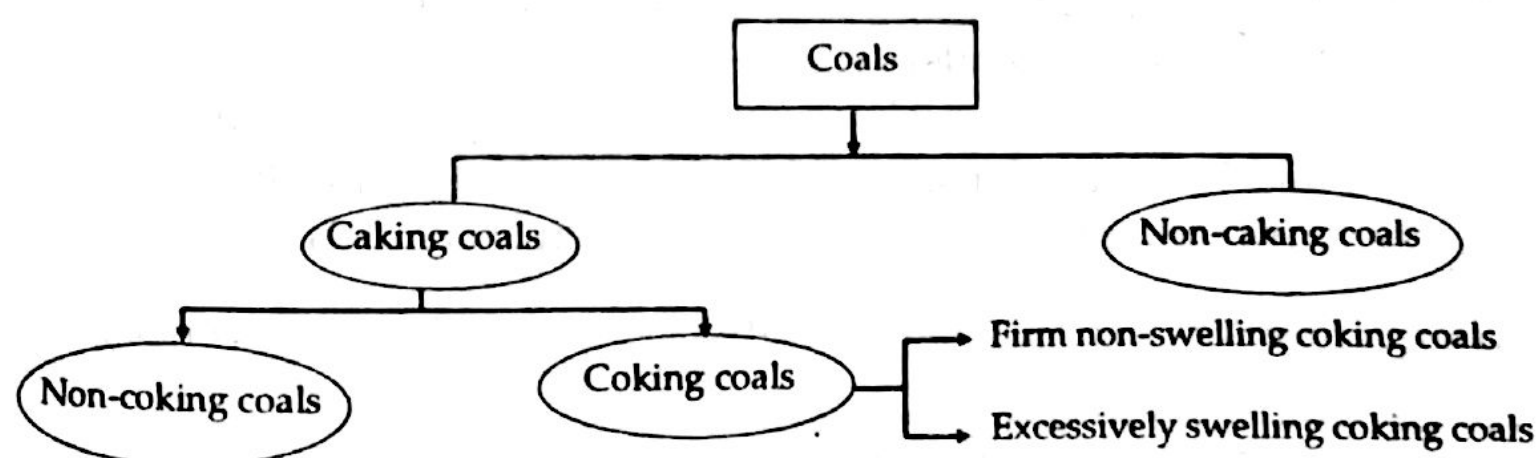


Depending on the behaviour of coal, when it is heated in the absence of air, we can classify coal into following categories :

(i) *Non-coking coals*. Which undergo practically no fusing effect, such coals are also known as free-burning coals.

(ii) *Coking coals*. Such coals give Porous, hard and strong residue after heating in the absence of air. The residue is usable for metallurgical purposes and is known as coke. coking coals are suitable for metallurgical purposes, because they are quite strong and not crushed under the weight of ore, flux plus coal in big furnaces.

There are some coals which become soft, plastic and fuse together to form large coherent masses. Such coals are called *caking coals*. It is interesting to note that "all coking coals are caking, but all caking coals are not essentially coking coals."



However, anthracite, sub-bituminous coals and lignite coals are non-coking.

Generally, coking coals are of following two types :

(i) *Firm non-swelling coking coals*. These yield compact hard coke without any increase in the original volume. Therefore, they are used in blast furnaces.

(ii) *Excessively swelling coking coals*. They swell excessively when coke is formed from them. Therefore, they are not used in blast furnaces.

Thus, all types of coals cannot be converted into coke. Only that coal can be converted into coke which has a tendency to soften, swell and stick together during strong heating in the absence of air. This property is found only in bituminous type of coal and hence *only bituminous coal can be coked*.

Caking coals with high volatile matter content are used for gas manufacture whereas caking coals of somewhat lower volatile matter content are used for the manufacture of metallurgical coke and are thus termed as coking coals.

Non-caking coals do not produce a good coherent mass during heating in the absence of air. But their rate of carbonization is very high. Thus, practically, coking coals are blended with non-caking coals since it helps in increasing the rate of carbonization and producing a good quality coke from non-caking coal.

#### *Requisites of a Good Metallurgical coke*

(i) *Combustibility*. The coke should burn easily but at the same time should not be very reactive.

(ii) *Calorific value*. It should possess a high calorific value.

(iii) *Strength*. The mechanical strength of the coke should be very high. This is due to the fact that coke has to withstand the abrasion and over-burden of the ore, fuel and the flux in the furnace. If the strength is not sufficient, the coke will break into smaller particles during charging of the furnace. The smaller particles, in turn hinder the flow of gases and choke the air passages.

(iv) *Porosity*. For complete combustion at high rate, carbon of coke should easily come in contact with oxygen. This is possible only if the porosity of the coke is high. Hence coke should be porous.

(v) *Purity*. The best metallurgical coke should contain lowest possible percentages of :

- (a) *Moisture* because it lowers the calorific value and increases the heating expenses.
- (b) *Ash*. because it hinders the heating process, lowers the calorific value and lead to slag formation.
- (c) *Sulphur and phosphorus*. Because they give undesirable products like  $\text{SO}_2$  and  $\text{P}_2\text{O}_5$  which contaminate the metal being produced. Moreover, brittleness of coke is due to the presence of sulphur.

(vi) *Calorific intensity*. The calorific intensity of coke should be high enough to melt the metal.

#### **10 TYPES OF CARBONIZATION OF COAL**

Depending on the temperature of carbonization, there are two types of carbonization viz. Low-temperature and high-temperature carbonization.

(A) *Low-temperature carbonization*. It is done at  $500 - 700^\circ \text{C}$  and is mainly carried out for the manufacture of domestic fuel.

(B) *High-temperature carbonization*. It is done at  $900 - 1200^\circ \text{C}$  and is mainly carried out for the manufacture of metallurgical coke.

Table 5 gives a comparative account of the characteristics of low temperature and high temperature carbonization.



**Table 5 : Characteristics of Low and High Temperature Carbonization**

S. No.	Characteristics	Low Temperature Carbonization	High temperature Carbonization
1.	Heating temperature	About 500 – 700° C	900 – 1200° C
2.	Yield of coke	75 to 80%	65 to 75%
3.	Volatile matter content in coke	5 to 15%	1 to 3%
4.	Mechanical strength of coke	Poor	Good
5.	Calorific value of gas	About 6500 to 9500 kcal/m <sup>3</sup>	About 5400 to 6000 kcal/m <sup>3</sup>
6.	Quantity of by-product gas produced	About 130 – 150 m <sup>3</sup> /tonne	About 300 – 390 m <sup>3</sup> /tonne
7.	Coke produced is	Soft	Hard
8.	Smoke produced on burning coke	Smokeless	Smoky
9.	In gas, % of		
	(a) Aromatic hydrocarbons	Lower	Higher
	(b) Straight-chain hydrocarbons	Higher	Lower
10.	Use of coke	For domestic purposes	For metallurgical purposes.

**Table 6 : Process of carbonization w.r.t. Temperature**

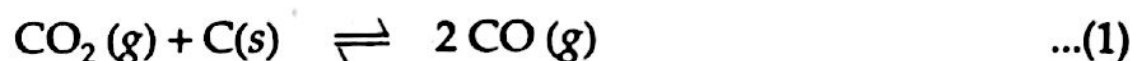
Temperature of bituminous coal bed	Process remarks
9. 1000°C – 1200°C	<b>High temperature carbonization</b> occurs and metallurgical coke is produced.
8. 700°C – 900°C	<b>Medium temperature carbonization</b> occurs and yields of total light oils and phenols (particularly cresol) are more.
7. 500 – 750°C	<b>Low-temperature carbonization</b> occurs and valuable, smokeless domestic fuel is produced
6. 700°C	Increase in the amount of liberated hydrogen occurs.
5. T < 450°	Liberated gases mainly comprise of hydrocarbons.
4. 350° – 450°C	Along with decomposition, coal also melts and become plastic.
3. 350°C	Active decomposition of the coal occurs alongwith brisk evolution of gas and tarry vapours.
2. 270°C	Some H <sub>2</sub> S and olefin gases are evolved.
1. T < 200°C	Moisture and occluded gases are driven out first.

**Reactivity and Uses of Coke****(a) Reactivity of coke towards oxygen.**

- Coke should be reactive to oxygen when *heat production* is important as in foundries.
- The ease of reaction (or reactivity) to oxygen or *combustibility* of coke improves by the presence of iron compounds, such as ferric oxide or ferric chloride, in coke, probably because these iron compounds catalyze the oxidation of coke to CO<sub>2</sub>.
- At a given temperature, cokes derived from LTC are more combustible compared to ones derived from HTC
- Cokes derived from weakly caking or blends of caking and non-caking coals are more combustible compared to those cokes which are derived from strongly caking coals.

**(b) Reactivity of coke towards carbon dioxide.**

- When a coke has low reactivity, especially to CO<sub>2</sub>, it can easily preserve its identity and by its combustion, coke is able to provide enough heat.
- The reactivity towards CO<sub>2</sub> is the extent to which reduction of CO<sub>2</sub> occurs as represented by equation (1) and is important in *producer gas manufacture*.



- Cokes produced by high temperature carbonization (HTC) are less reactive towards CO<sub>2</sub> than the low-temperature carbonized (LTC) ones.
- At a given temperature, coke containing inorganic compounds like Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> etc. are more reactive towards CO<sub>2</sub>, but at higher temperatures the reactivity decreases.

**(c) Reactivity of coke towards steam.**

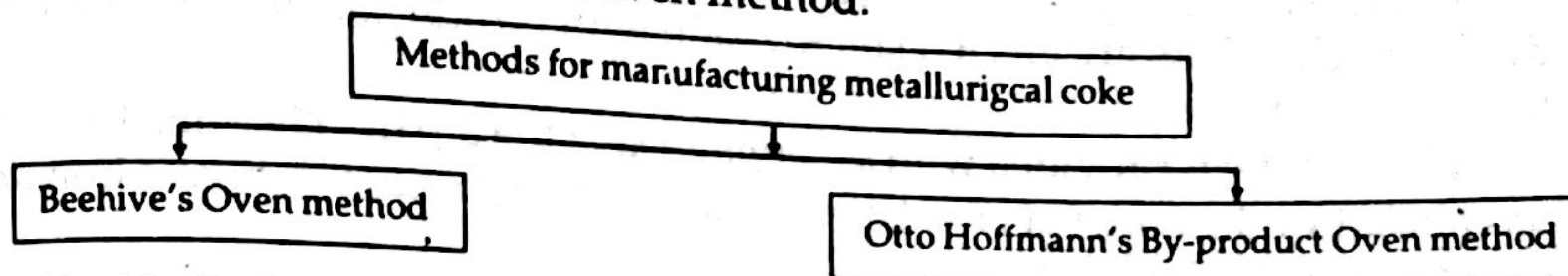
- Reactivity to steam is expressed as the percentage of steam decomposed in reactions (1) and (2) below :

S.No.	Reaction	$\Delta H$ (kCal)
1.	$\text{C} (\text{s}) + \text{H}_2\text{O} (\text{g}) \rightleftharpoons \text{CO} (\text{g}) + \text{H}_2 (\text{g})$	+ 31
2.	$\text{C} (\text{s}) + 2\text{H}_2\text{O} (\text{g}) \rightleftharpoons \text{CO}_2 (\text{g}) + 2\text{H}_2 (\text{g})$	+ 19

- For *water-gas manufacture*, the coke must be reactive to steam.
- Reactivity to steam follows the same trend as that of CO<sub>2</sub> viz.
  - reactivity varies inversely with carbonizing temperature at which the coke was produced.
  - cokes from non-caking coals are more reactive than those from caking coals.

## 11 MANUFACTURE OF METALLURGICAL COKE

Metallurgical coke can be made by two methods viz. Beehive's oven method and Otto Hoffman's by-product oven method.



### 11.1 Beehive's Oven Method

It is the earliest and most economical method for the manufacture of metallurgical coke.

**Construction of Beehive oven.** The Beehive's oven is dome-shaped structure made of bricks. It is about 4 m wide and 2.5 m high. It has two openings, one at the top for the charging of coal and the other at the side through which the coke formed is removed. This side opening also acts as inlet for air supply as and when desired.

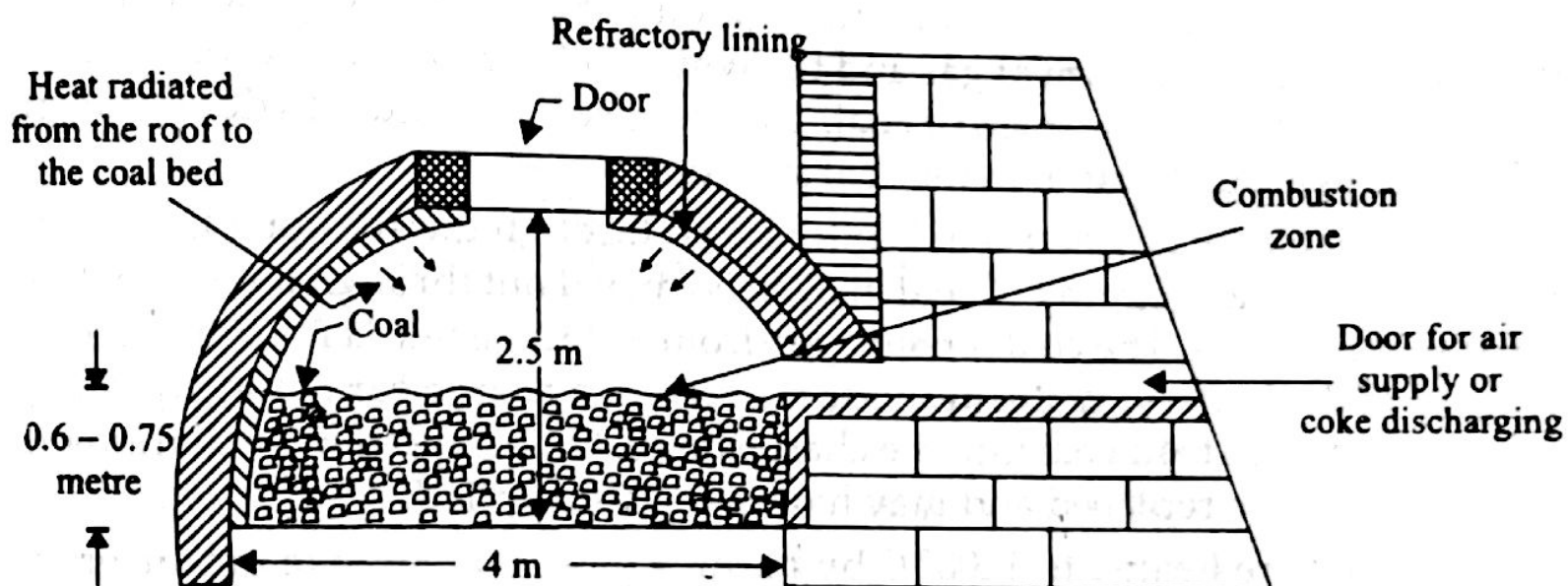


Fig. 9. Beehive oven.

**Process.** From the top opening, the coal is charged to give a layer of about 0.6 – 0.75 m thick coal. Some air is supplied in from the side opening and the coal is ignited. This partial combustion furnishes heat which melts or fuses the coal and the evolved volatile matter burns at the partially closed side opening. Combustion is allowed to proceed in a gradually diminishing supply of air so that slow carbonization from the top layer to the bottom layer, takes place. This process of carbonization completes in about 3-4 days. The hard metallurgical coke formed is quenched with water and taken out from the discharge side opening. The yield of coke is about 60-80 % of the coal charged and averages about 5 – 6 tonnes of coke per oven.

It is possible to make this process more economical by operating a series of Beehive's ovens in such a way that hot gases escaping from an oven are utilized to ignite the charge in the adjacent oven.

#### Limitations of Beehive's oven method

- (i) Most of the volatile matter having plenty of valuable chemicals escapes out into the atmosphere as waste. This also creates problems of air pollution.
- (ii) Due to partial combustion, coke yield is less.
- (iii) Operational flexibility is not there in Beehive's oven method.



### 11.2 Otto Hoffmann's By-product Oven Method

**Construction.** The by-product coke oven consists of a number of narrow *silica chambers*. Each chamber is about 10-12 meter long, 3-4 meter high and 0.40-0.45 m wide. These chambers are erected side-by-side with *vertical flues* in between them to form a sort a battery.

Each chamber is provided with a *charging hole* at the top (for charging the coal), a *gas off take* (for the removal of volatile matter) and a refractory line cast iron *door* at each end (for discharging coke).

**Theory.** Coking processes are always carried out in narrow retorts or ovens, which are heated from both sides because coal is poor conductor of heat. The coals adjacent to the oven walls get heated and the plastic zone formed in the case of caking coals moves away from the walls towards the central zone. The plastic zone though mobile is such a bad conductor of heat that while the inner zones are getting heated, the semi-coke at the outer zones would have been converted into coke.

The coking is accompanied by a contraction in volume.

The contraction at lower temperatures (around  $500^{\circ}\text{C}$ ) corresponds to the loss of volatile matter in the form of gas and tar, while that at  $750^{\circ}\text{C}$  corresponds to the solidification of the plastic mass of coal. This has been attributed to dehydrogenation leading to aromatization in the coal structure.

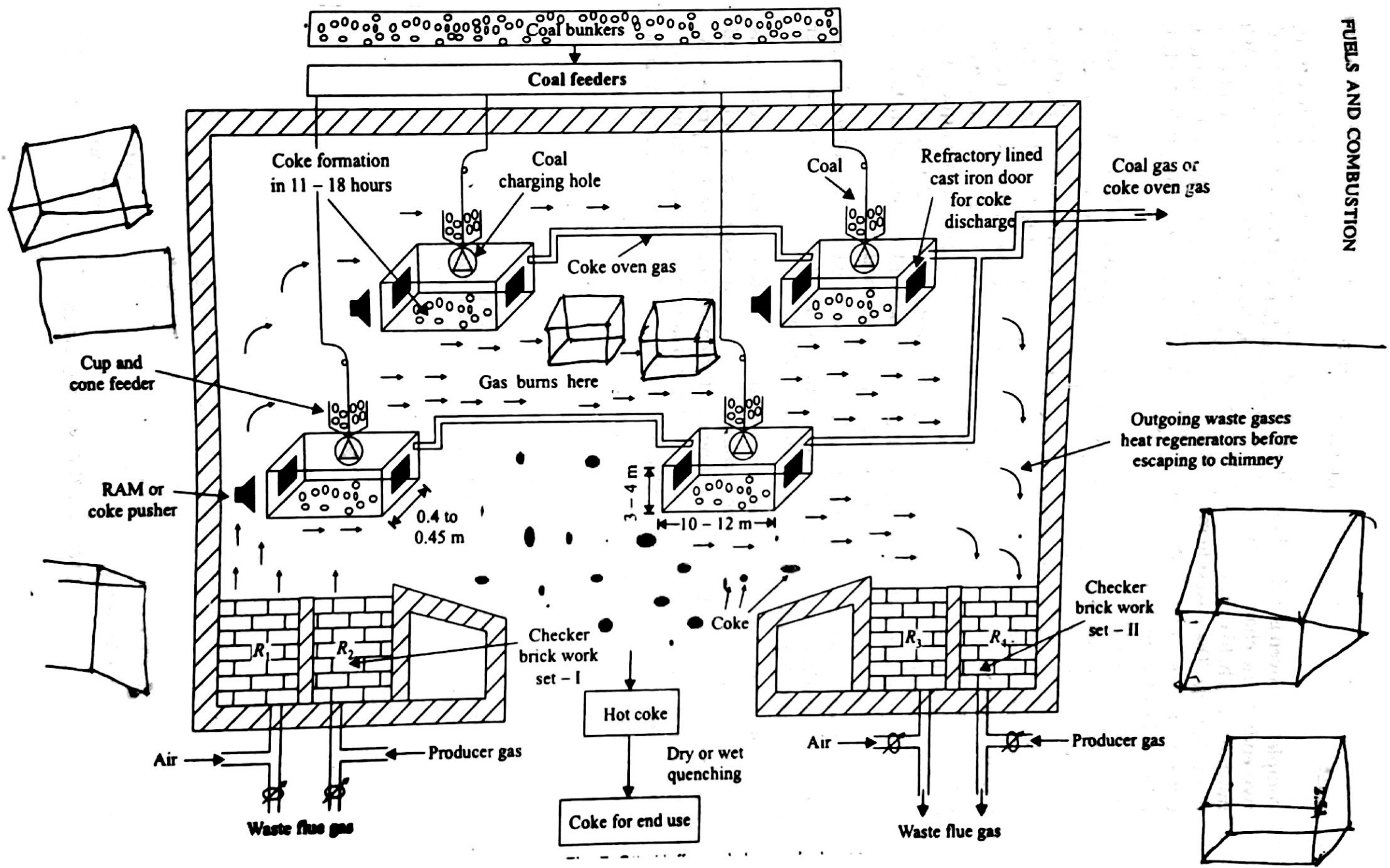
**Working.** Finely crushed coal is introduced through the charging holes at the top of chamber. The charging of coal in oven is carried out through a series of holes in the top of the oven. The coal is conveyed from a storage bunker, usually located at the end of the battery, to the individual ovens in a charge car having discharge orifices designed to feed coal into the charge holes. On completion of charging the charge hole lids are replaced and may have a sealant applied.

The ovens are heated to  $1200^{\circ}\text{C}$  by burning gaseous fuel (like producer gas) and usually employing a *regenerative principle* to achieve as economical heating as possible (utilizing the waste flue gases for heating the checker-work of bricks). The flue gases produced during combustion, before escaping to chimney, pass on their sensible heat to one of the two sets of checker brick-work, untill this brick-work has been raised to a temperature of about  $1000^{\circ}\text{C}$ . The inlet gases are passed through the heated checker brickwork, which thus serves to preheat the inlet gases. While the flue gases leave their acquired heat to one generator, the other generator is used for preheating the incoming air.

During the first phase of cycle, producer gas and air are separately passed through previously heated regenerators  $R_1$  and  $R_2$  (checker brick work set-I) while the products of combustion (hot flue gases) flow through the regenerators  $R_3$  and  $R_4$ . The rapid combustion takes place because the gases have been preheated to high temperature. Subsequently, the process is reversed. Every few minutes, the direction of gases is reversed so that incoming gases are always preheated. This *regenerative principle of heat economy* was proposed by William Siemens in 1857.

It is enough if air is preheated in the case of a fuel (coal gas) with high calorific value but if the calorific value of the fuel is low (producer gas, blast furnace gas), both the fuel and combustion air are preheated.

The heating is continued, untill all the volatile matter has escaped. It takes about 11-18 hrs, for carbonization of a charge of coal. When carbonisation is



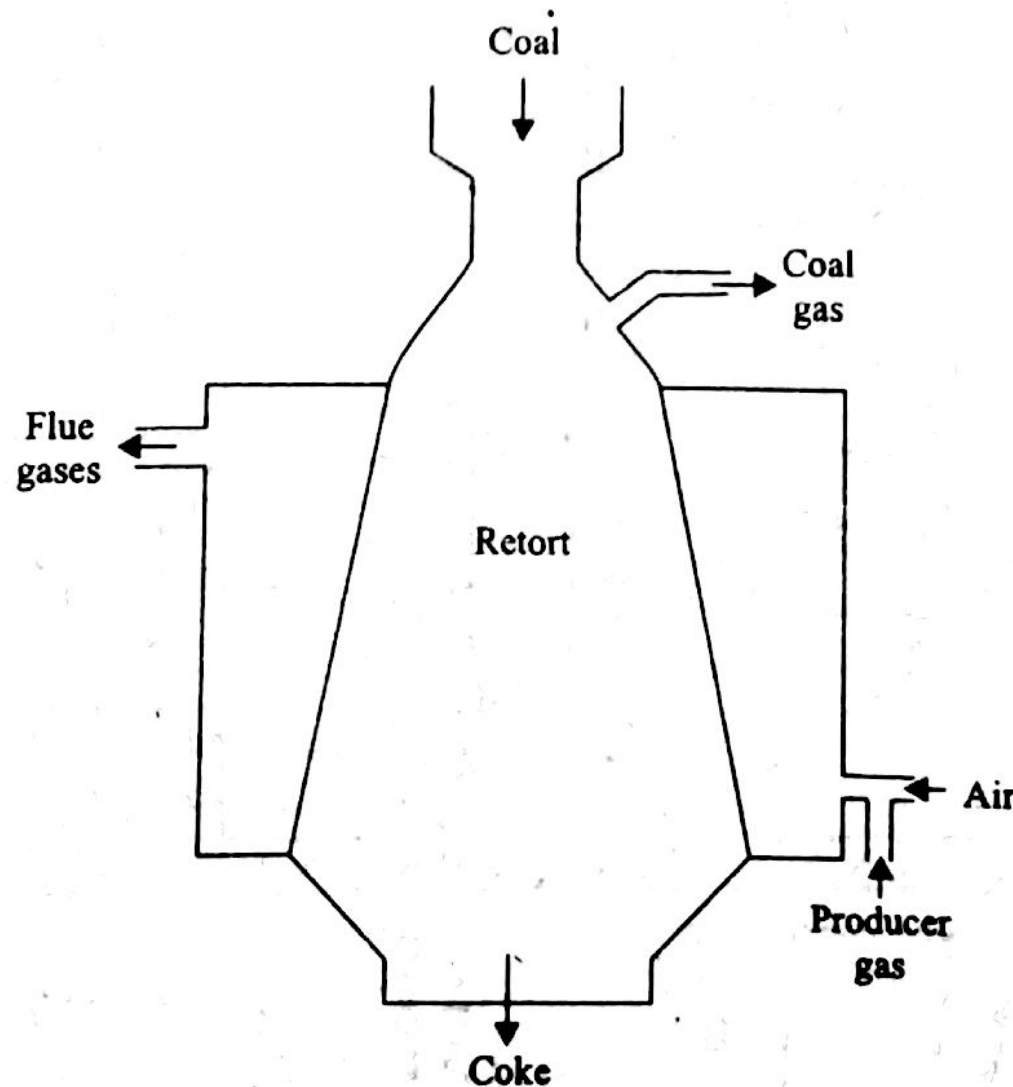
complete the oven is isolated from the collector main and the doors which form the two ends of the chamber are removed by the pusher machine and the coke side machine which, like the charge car, are designed to travel up and down the length of the battery. The cokeside machine places a coke guide against one end of the oven and a ram mounted on the pusher machine pushes the coke through the guide into a coke collecting car. The ovens have slight taper towards the pusher side to ease oven discharge.

The coke-collecting car transports the hot coke to a quench tower where water is sprayed on it before it is discharged on an inclined bench known as coke wharf.

An alternative way of cooling the coke is to charge it into a vertical shaft via a lock hopper system and allow it to descend counter-current to a cooling inert gas flow before discharge through a second lock hopper. The heat absorbed by the gas is used for steam raising or other purposes and in most installations the gas is re-cycled. This is known as coke dry quenching (CDQ). In place of wet quenching "dry quenching" offers advantages, because the coke produced is more strong, dense, graphitized and non-reactive. The coke produced by 'dry-quenching' is cheaper, drier and contains lesser dust than 'wet-quenched' coke.

These days, *vertical retorts* of rectangular cross-section tapering outwards from top to bottom are in use for coal gas production. They can be operated either intermittently [Fig. 10(i)] or continuously [Fig. 10(ii)].

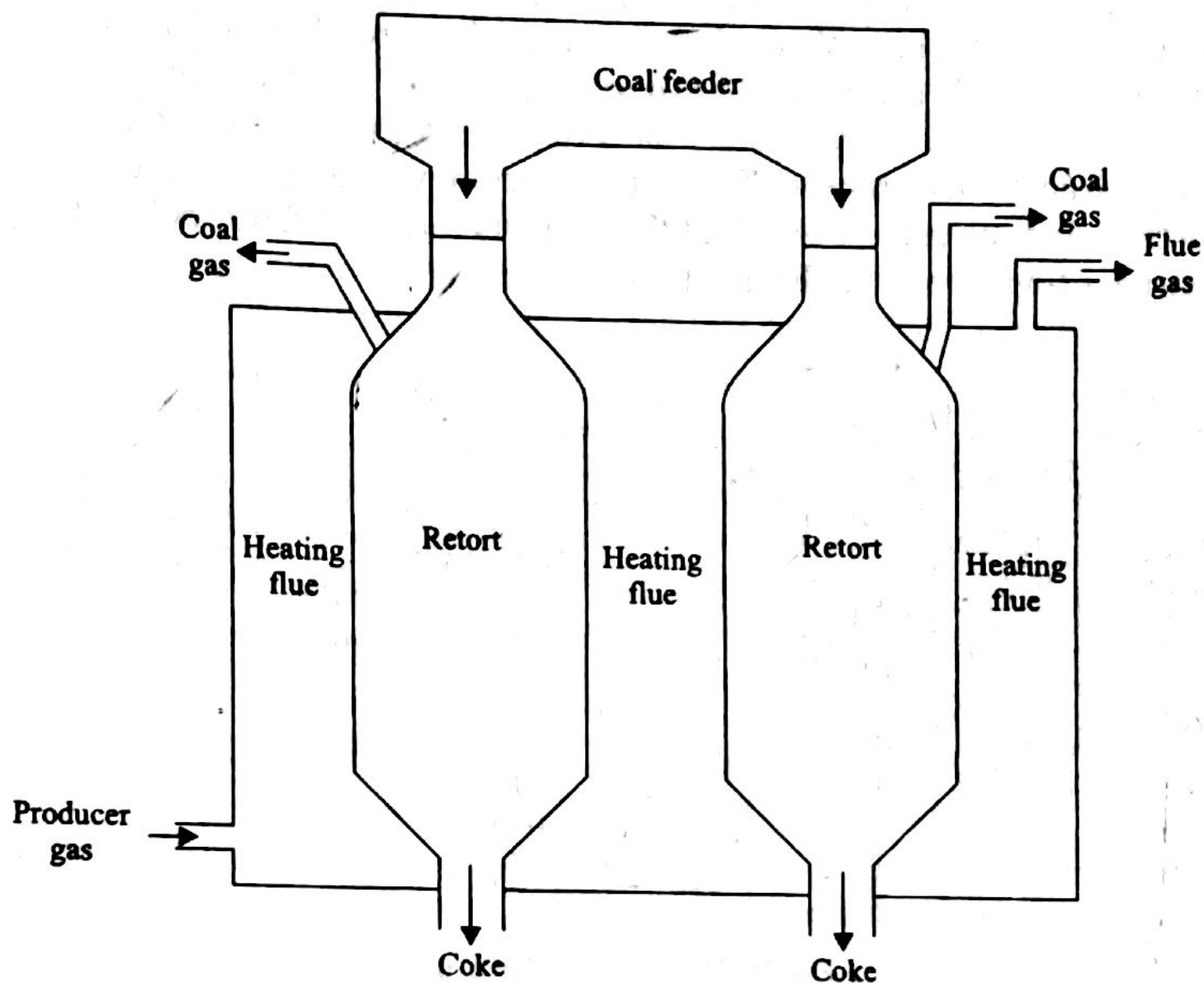
In the *intermittent type vertical gas retort*, coal is heated by burning producer gas with preheated air in heating flues arranged between the retorts. Steam is passed into the retort for about 2 to 3 hours towards the end of carbonization process. By the reaction between coke and steam, water gas is produced, consequently, the overall yield of the gas increases. Steam also prevents the formation of graphitic deposits on the walls of the retort.



(i) Intermittent type vertical gas retort.

...(1)





(ii) Continuous type vertical gas retort.

Fig. 10. Diagrammatic representation of gas retorts.

In the *continuous type vertical gas retort*, the coal to be carbonized is fed at the top of retorts and collected as coke from the bottom. The retorts are either cylindrical or oval in cross-section. As in the former process,

- (i) retorts are heated by producer gas,
- (ii) Steam is continuously blown into the retort to quench the coke, and expelling the volatile matter before they can undergo cracking, and
- (iii) Overall yield of gas is greater due to the formation of water gas.

#### Essential steps of the coke-making process :

- (i) Bituminous coal is fed into a series of ovens, which are sealed.
- (ii) Ovens are heated at high temperatures in the absence of oxygen, for 14 – 36 hours.
- (iii) Volatile compounds that are driven off the coal are collected and processed to recover combustible gases and other by-products.
- (iv) The solid carbon remaining in the oven is *coke*. It is taken to the quench tower, where it is cooled with a water spray or by circulating an inert gas like nitrogen, a process known as *dry quenching*.
- (v) The coke is screened and sent to a blast furnace or to storage.

**Recovery of by-products.** The gas coming out from the oven is known as '*coke oven gas*'.

The coal gas thus obtained is impure. It contains number of valuable impurities like tar, ammonia, benzol, naphthalene and hydrogen sulphide. The by-products are removed from the coal gas to improve the quality of gas. These by-products also have their utility value. The gas is first scrubbed by passing through a hydraulic main, which acts as a water seal. The scrubbing removes some tar and water soluble products such as ammonia. Much of the tar is then removed by cooling the gas in condenser (a huge water cooled heat exchanger).

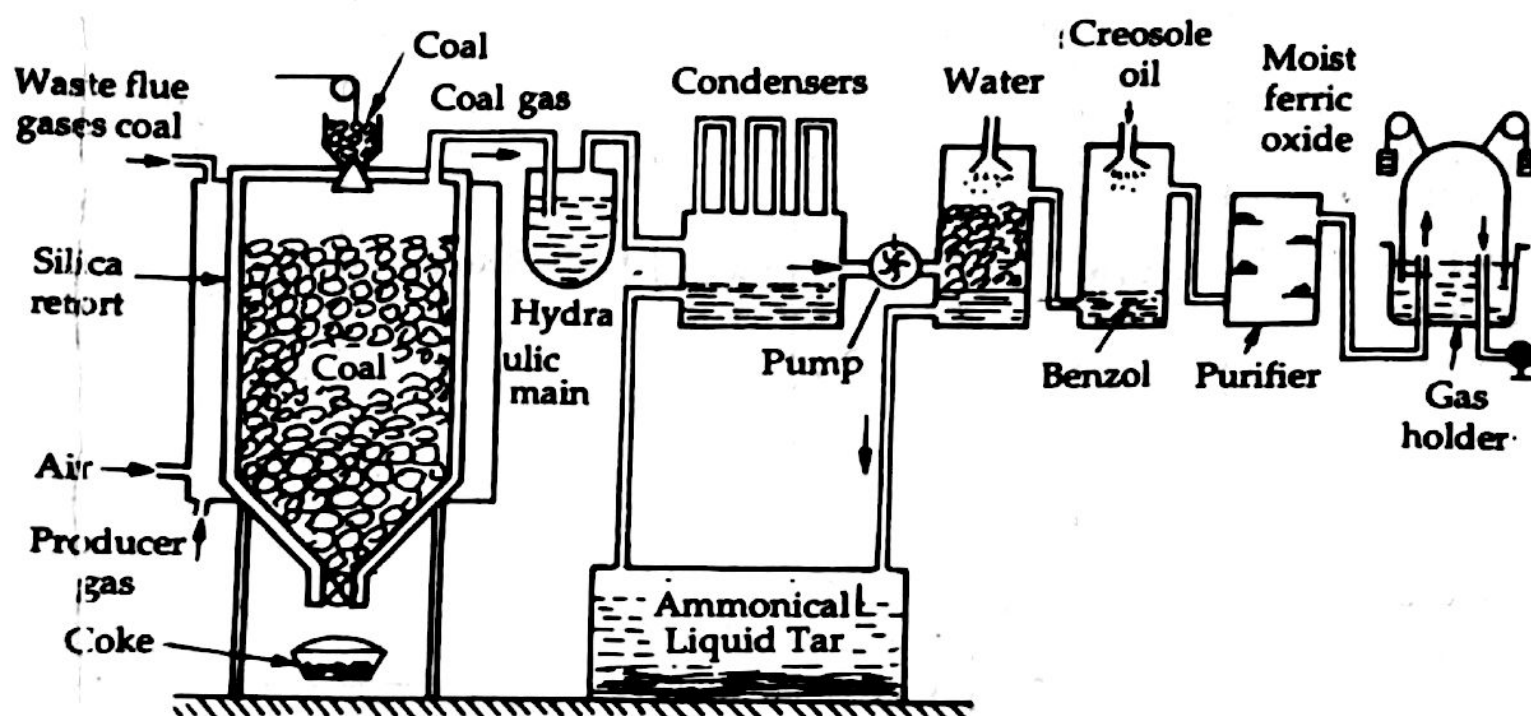


Fig. 11. Manufacture of coal gas.

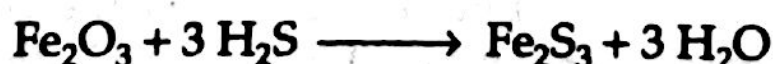
(i) *Recovery of tar.* The gas is first passed through a tower in which liquid ammonia is sprayed. Here dust and tar get collected in a tank below, which is heated by steam coils to recover back ammonia sprayed. The ammonia is used again.

(ii) *Recovery of ammonia.* The gases from the chamber are then passed through a tower in which water is sprayed. Here ammonia goes into solution as  $\text{NH}_4\text{OH}$ .

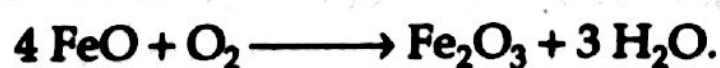
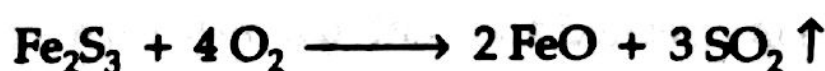
(iii) *Recovery of Naphthalene.* The gases are then passed through another tower in which  $\text{H}_2\text{O}$  is sprayed at low temperature when naphthalene gets condensed.

(iv) *Recovery of benzene.* The gases are then sprayed with petroleum when benzene and its homologues can be recovered.

(v) *Recovery of  $\text{H}_2\text{S}$ .* The gases are then passed through a purifier, packed with moist  $\text{Fe}_2\text{O}_3$ . Here  $\text{H}_2\text{S}$  is retained.



After some time, when all  $\text{Fe}_2\text{O}_3$  is changed into  $\text{Fe}_2\text{S}_3$ , the purifier is exposed to atmosphere ; so that  $\text{Fe}_2\text{O}_3$  is regenerated.



### Significance of recovery of By-products :

**Coke-Oven gas** contains large no. of valuable impurities. These are removed from the coal gas mainly because of their utility value and also to improve the quality of the gas.

**Tar.** Tar pitch is used for road making and for preserving timber. Tar on fractional distillation gives benzene, toluene, naphthalene, cresote oil, etc ; which are the starting materials for obtaining numerous drugs, perfumes and explosives.

**Ammonia.** The removal of ammonia from the gas is necessary to avoid the blockage of gas pipes by ammonium carbonate.

$\text{NH}_3$  is removed by absorption in water in a scrubber or dissolved in dil.  $\text{H}_2\text{SO}_4$  to form ammonium sulphate which is used as a fertilizer.

**Naphthalene.** Naphthalene and other higher aromatics, present in tarry vapours, may cause blocking of the gas pipes.

**Benzene.** (and Toluene and xylenes) : These are industrially important solvents and raw materials for plastics.

**$\text{H}_2\text{S}$ .**  $\text{H}_2\text{S}$  and other S compounds present in coal may give a foul smell (offensive odours) to the gas.

S compounds may get oxidized to  $\text{SO}_2$  and finally to  $\text{H}_2\text{SO}_4$  which promotes corrosion.

### 11.3 Coal Gas

Coal gas is lighter than air and is colourless gas. It has a characteristic odour and burns with a smoky flame. Its *average composition* is :

Constituent	$\text{H}_2$	$\text{CH}_4$	$\text{CO}$	$\text{C}_2\text{H}_2$	$\text{C}_2\text{H}_4$	$\text{N}_2$	$\text{CO}_2$	Rest
Percentage	40%	32%	7%	2%	3%	4%	1%	4%

The calorific value of coal gas is about  $4,900 \text{ kcal/m}^3$ .

**Production.** When coal is carbonized (heated in the absence of air) at about  $1300^\circ\text{C}$  in either gas making retorts or coke ovens, coal gas is obtained.



With the help of cup and cone feeder, powdered coal is fed from the top into the large, vertical, silica retorts. The retorts are heated externally (by burning a mixture of producer gas and air) to about  $1300^\circ\text{C}$ .

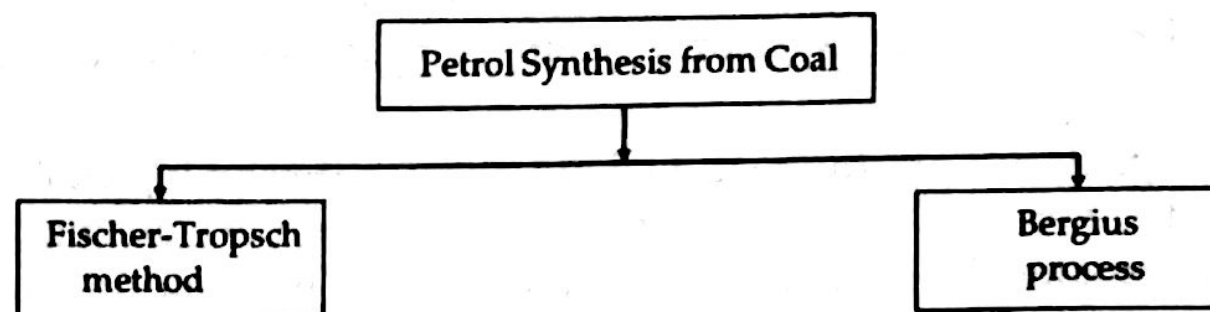
The purified coal gas is finally stored over water in gas holders.

**Applications.** Coal gas is used as (a) a fuel ; (b) for providing reducing atmosphere in many metallurgical operations ; and (c) illuminant in cities and towns.



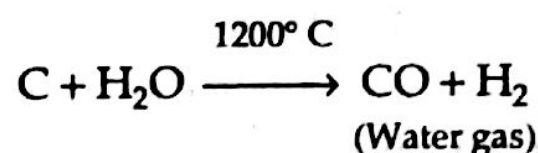
## 12 CONVERSION OF COAL INTO LIQUID FUELS

Petrol is synthesized by any one of the following methods :



### 12.1 Fischer-Tropsch Method

The raw material is the hard coke which is converted into water gas ( $\text{CO} + \text{H}_2$ ) by passing steam over red hot coke.



A mixture of hydrogen and water gas ( $\text{CO} + \text{H}_2$ ) is first purified by passing through  $\text{Fe}_2\text{O}_3$  (to remove  $\text{H}_2\text{S}$ ) and then into a mixture of  $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3$  (to remove organic sulphur compounds).

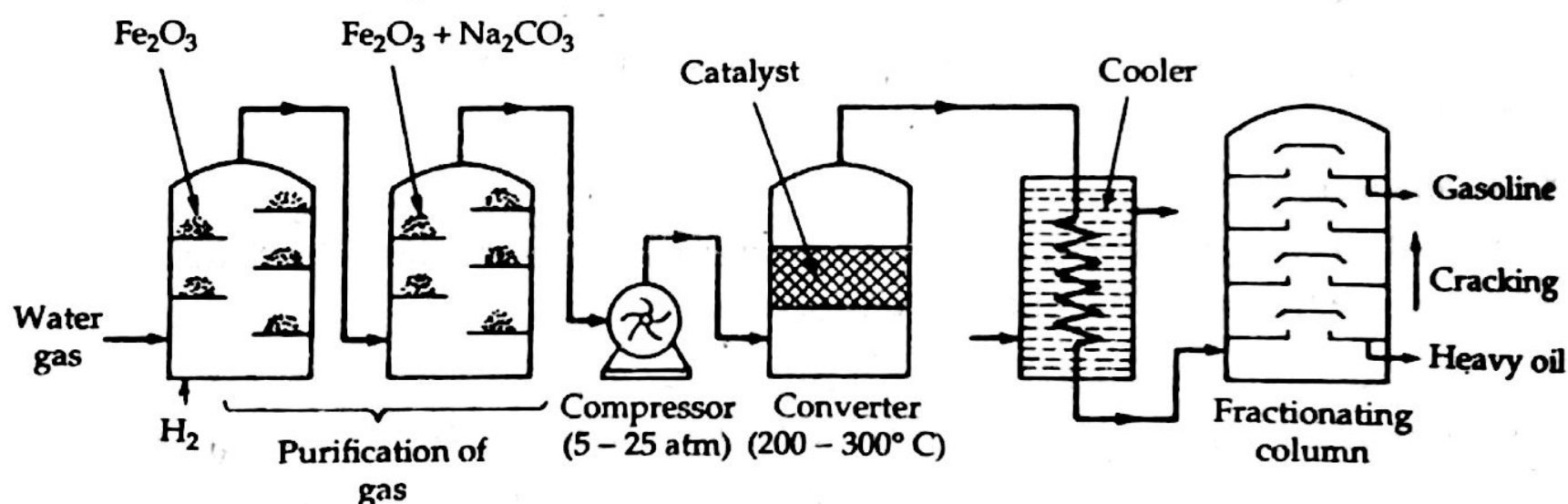
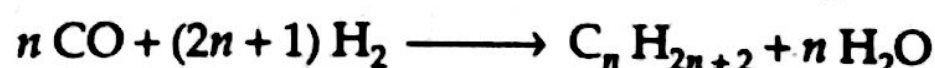
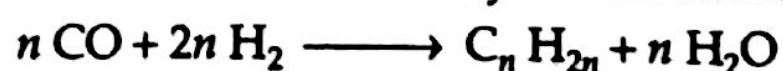


Fig. 12. Fischer-Tropsch Method

The purified gas is compressed to 5 to 25 atm and then passed through a convertor maintained at about  $200 - 300^\circ \text{C}$ . The convertor is packed with a catalyst, consisting of a mixture of

Cobalt (Co),	Thoria (Th),	Magnesia ( $\text{MgO}$ )	and Keiselguhr earth
100 parts	5 parts	8 parts	200 parts

A mixture of saturated and unsaturated hydrocarbon results :



The outcoming hot gaseous mixtures from the exothermic reaction are led to a cooler, where a liquid resembling crude oil is obtained.

The crude oil thus obtained is then fractionated to yield :

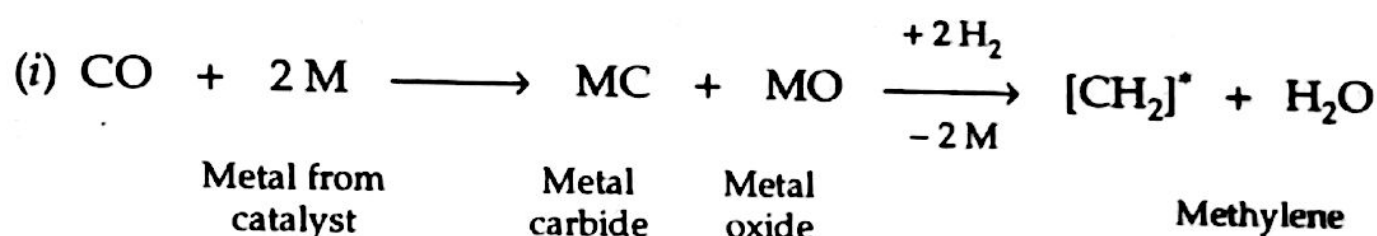
- (i) gasoline and
- (ii) High-boiling heavy oil.

The heavy oil can be reused for cracking to get more gasoline.

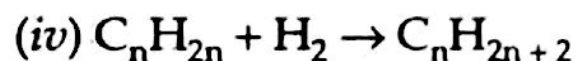
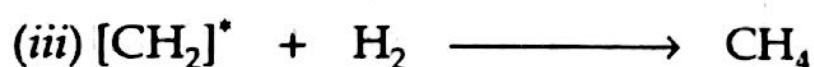
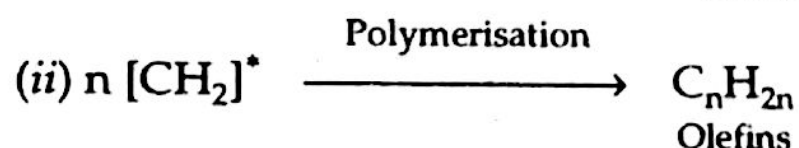
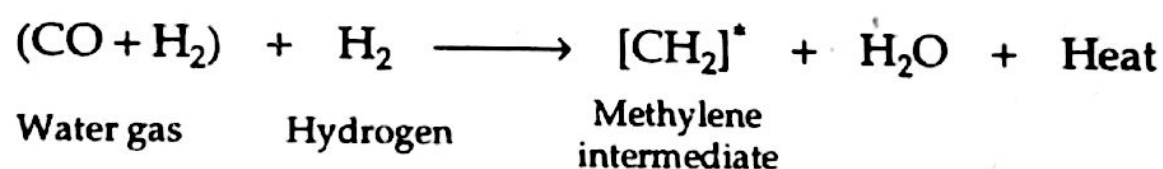
- The general stages in the Fischer-Tropsch synthesis can be represented as follows :

1. Synthesis gas production.
2. Purification of synthesis gas by removal of dust, H<sub>2</sub>S and organic sulphur compounds.
3. Conversion of synthesis gas into mixture of saturated and unsaturated hydrocarbons in catalytic converter.
4. Cooling and condensation of products.
5. Fractional distillation to get gasoline.

- The Mechanism of Fischer-Tropsch Process may be represented as follows :



Or



The catalyst based on Fe, Co, Ni metals seems to function mainly through the formation of an intermediate surface oxygen complex.

Reduction of metallic carbide accounts for only 10 to 15% of the hydrocarbons. The carbide of the metal was supposed to be formed on the catalyst surface and this carbide subsequently hydrogenated to give various hydrocarbons.

With Ru as catalyst, first alkyl Ruthenium carbonyls are formed as intermediate, which then on hydrogenation at high temperatures give hydrocarbons. For the formation of Ruthenium carbonyl, CO is chemisorbed on the metal surface.

- In Fischer-Tropsch method, the nature of the product is determined by temperature, pressure and the nature of the catalyst.

(A) (i) Nickel catalyst gives a product mainly consisting of gasoline and fuel oil.

(ii) A cobalt catalyst gives more olefins.

(iii) Mixed catalysts such as cobalt-magnesia are used to produce high-grade diesel fuel.

(B) Iron oxide with K<sub>2</sub>CO<sub>3</sub> as promoter gives heavier hydrocarbons than what are obtained from iron oxide and Na<sub>2</sub>CO<sub>3</sub>.

(C) (i) With oxide catalysis such as ZnO- Cr<sub>2</sub>O<sub>3</sub> at temperatures of 200° – 400°C and pressures of 100 – 1000 atm, methanol and other alcohols are the main products.

(ii) With  $\text{ThO}_2$  or  $\text{ZnO} - \text{Al}_2\text{O}_3$  catalyst, *hydrocarbons* are the main products.

(iii) With  $\text{Ru}$  catalyst, *higher hydrocarbons* are the main product.

(D) When the Fischer-Tropsch process is carried out under pressure, a higher amount of diesel fuel and waxes are obtained at the expense of gasoline which, because of its low octane number requires upgrading by mixing with benzole.

The Fischer-Tropsch process is mainly employed as a source of hydrocarbons for chemical production (in Germany). This is because inspite of using cheap raw materials (steam and coke), the process cannot compete economically with petroleum as a source of gasoline.

The few end uses are summarized below :

(i) Heavy oil after hydrogenation is used for the production of *detergents* (sodium alkyl sulphonates).

(ii) Soft waxes are oxidised by air at  $100 - 120^\circ\text{C}$  in the presence of small amount of  $\text{KMnO}_4$  as catalyst to *fatty acids*.

Higher fatty acids are used for (a) production of *synthetic fat* and (b) *soap manufacture*.

(iii) The hard waxes are used for the *conventional uses*.

- The Fischer-Tropsch process was devised on Germany in 1925.

## 12.2 Bergius Process

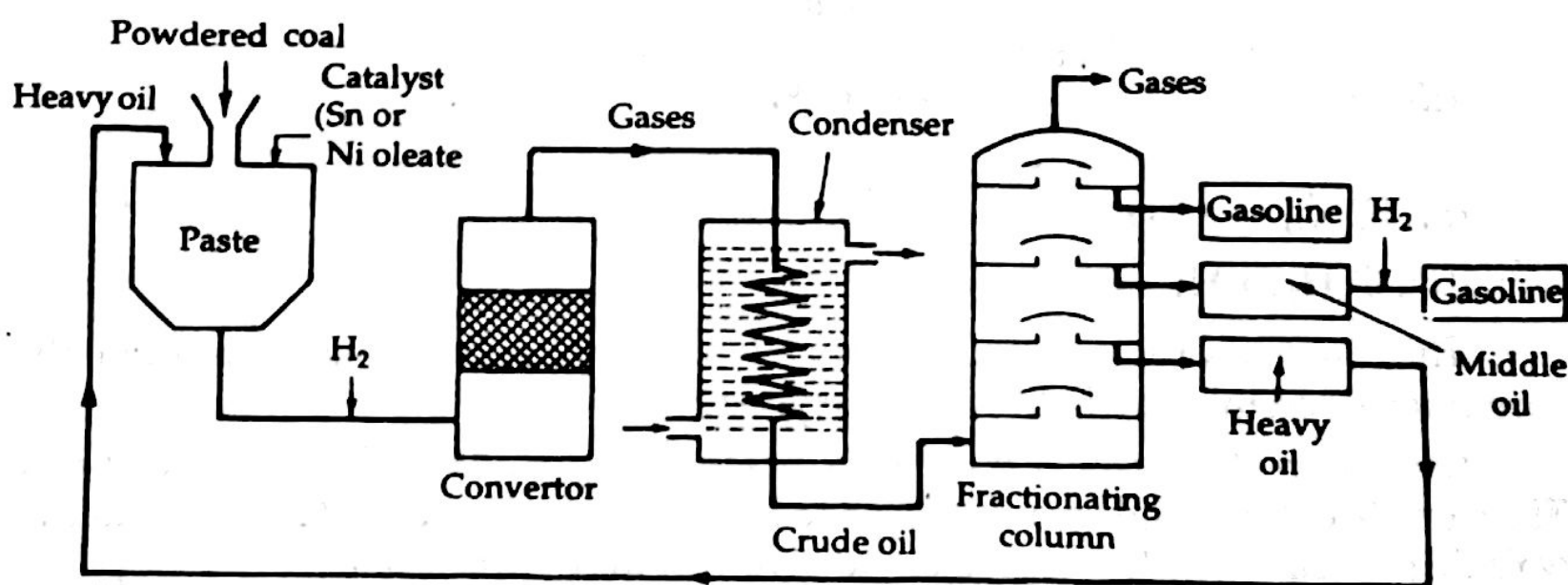


Fig. 13. Bergius process of hydrogenation of coal to gasoline.

Coal (which is a mixture of high molecular weight, complex organic compounds deficient in hydrogen) is a raw material in Bergius process.

In this process, the low ash coal is powdered well and made into a paste with heavy oil and catalyst (composed of tin or nickel oleate) is incorporated.

The paste is heated with hydrogen at  $450^\circ\text{C}$  and 200-250 atm. pressure for about 1.5 hours. The coal undergoes hydrogenation to form saturated hydrocarbons, which decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons.

The issuing gases (from the reaction vessel) are led to condenser, where a liquid resembling crude oil is obtained.

This liquid is then fractionated to get :

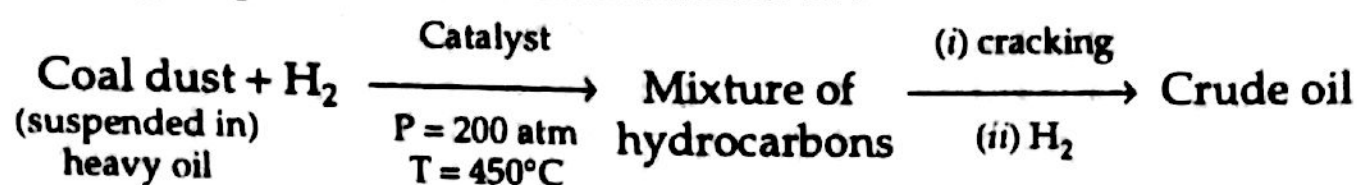
- (i) Gasoline,                      (ii) Middle oil, and                      (iii) Heavy oil.



Heavy oil is used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapour-phase in presence of a solid catalyst to yield more gasoline.

The yield of gasoline is about 60% of the coal dust used.

- The Bergius process can be summarized as :



- Bergius process is very important. One ton of soft coal produces 140 gallons of gasoline by this method.
- Hydrogenation of coal is not economical and can be adopted only by those countries having practically no oil but rich coal resources.

### 13 FLUE GAS ANALYSIS

The mixture of gases, mostly  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{O}_2$ , issuing out of the combustion chamber is called *flue gas*. The analysis of a flue gas either from a furnace or from an engine's exhaust would give an idea about the efficiency of the combustion process. If the flue gas contains considerable amount of  $\text{CO}$ , it indicates that incomplete combustion is occurring and it also indicates the short supply of  $\text{O}_2$  for combustion. This will lead to wastage of fuel. If the flue gas contains considerable amount of  $\text{O}_2$ , it indicates that the  $\text{O}_2$  supply is in very much excess. Too much excess of air results in loss of heat. In ordinary furnaces, 50 – 100% excess air is generally supplied.

If the analysis shows the presence of appreciable amounts of  $\text{CO}$  and  $\text{O}_2$  it indicates that the combustion is non-uniform and irregular. This might be due to excess of air in some parts of furnace and insufficient air in some other parts.

#### Construction of Orsat's apparatus

The analysis of flue gases is carried out with the help of Orsat's apparatus. It consists of a horizontal tube. At one end of this tube, there is a three-way stop-cock and the other end is connected with a burette. The burette is graduated and surrounded by a water-jacket to keep the temperature of the gas constant during the experiment. The burette is connected in series to a set of three absorption bulbs, each through a separate stop cock. The lower end of the jacketed burette is further connected to a water reservoir with the help of rubber tube. The water level in the burette can be raised or lowered by raising or lowering the water reservoir containing water. The other end of horizontal tube which is connected to three-way stop cock is further connected to a U-tube. The U-tube is packed with fused  $\text{CaCl}_2$  and glass wool for drying flue gas and for avoiding the incoming of any smoke particles respectively.

The three absorption bulbs apart from having solutions for absorbing  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{CO}$  also filled with glass tubes, so that surface area of contacts between the gas and the solution is increased. The *first bulb* has potassium hydroxide solution and it absorbs only  $\text{CO}_2$ . The *second bulb* has alkaline pyrogallous acid and it can absorb  $\text{O}_2$  and  $\text{CO}_2$ . The *third bulb* contains ammoniacal cuprous chloride and it can absorb  $\text{CO}$ ,  $\text{O}_2$  and  $\text{CO}_2$ . For proper analysis, it is necessary that the flue gas is passed first through first bulb containing  $\text{KOH}$  where  $\text{CO}_2$  is absorbed. Then it is

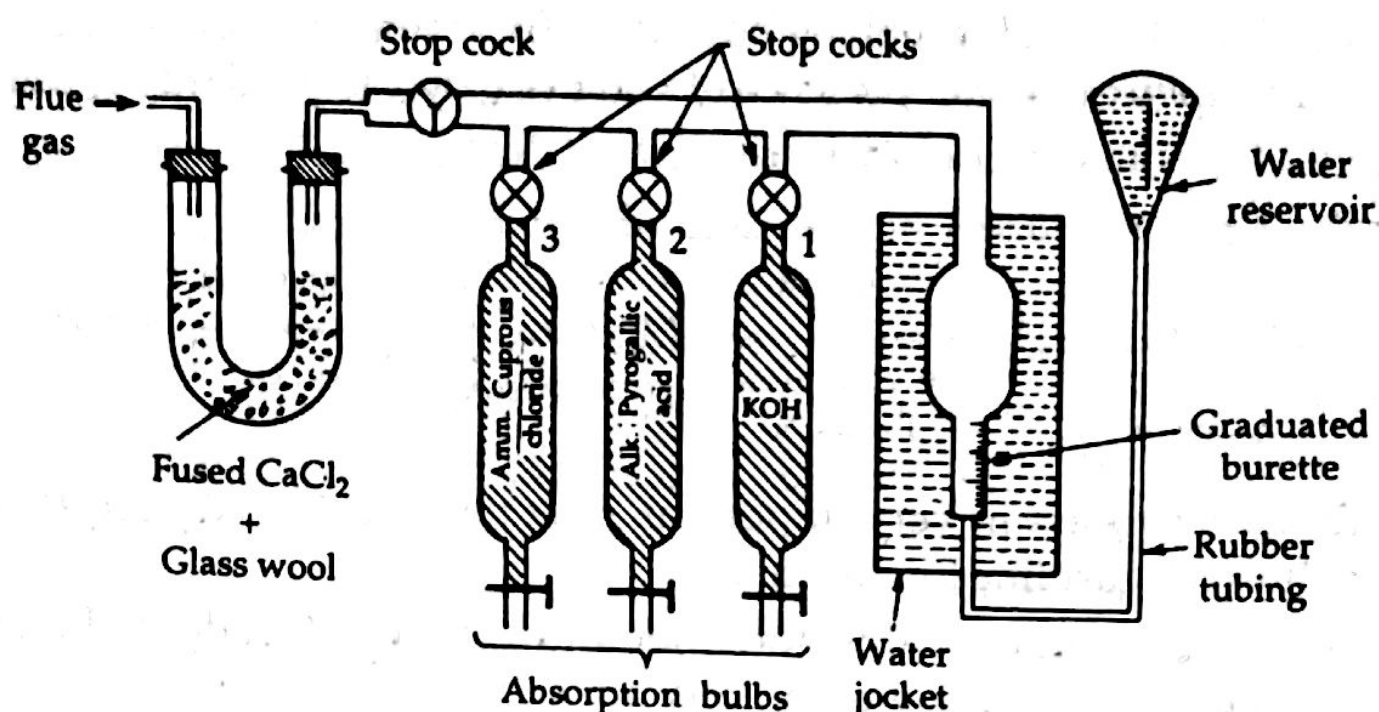


Fig. 14. Orsat's apparatus.

passed through second bulb containing alkaline pyrogallous acid, where only  $O_2$  will be absorbed. Although it can also absorb  $CO_2$  but all  $CO_2$  has already been removed by KOH. Finally, flue gases are passed through third bulb containing ammonical cuprous chloride, where only CO will be absorbed.

#### Working

- The whole apparatus is thoroughly cleaned, stoppers greased and then tested for air-tightness. The absorption bulbs are filled with their respective solution. Then their stop cocks are closed. The water reservoir and jacket are filled with water.
- Air is first excluded from the burette by raising the water reservoir till the burette is completely filled with water. For the exclusion of air, the three way stop cock should be opened to the atmosphere.
- Next, the flue gas to be analysed is drawn in by lowering the water reservoir and connecting the three way stop cock to flue gas supply.
- For better results, air from the capillary connecting tubes should be expelled by repeating the above process of sucking and expelling the flue gas by lowering and raising the water reservoir.
- Finally, 100 mL of flue gas is carefully sucked in the burette for analysis.

For adjusting final volume, the three-way stop-cock is opened to atmosphere and the water reservoir is carefully raised, till the level of water in it is the same as in the burette, which stands at 100 mL mark. The three-way stop-cock is then closed.

- The flue gas is forced in the bulb 1 by opening its stop cock and raising the water reservoir. Bulb 1 contains caustic potash solution which absorbs  $CO_2$ . For the complete absorption of  $CO_2$ , the flue gas is sent, 2 or 3 times, again and again in bulb 1. The unabsorbed gas is finally taken back in the burette and then stop cock for  $CO_2$  absorption bulb is closed. The levels of water in the reservoir and burette are equalised and the volume of residual gas is noted. The decrease in volume gives the volume of  $CO_2$  in 100 mL of the flue gas sample.



- The volumes of  $O_2$  and  $CO$  are similarly determined by passing the flue gas through absorption bulbs 2 and 3 respectively. The gas remaining in burette after absorption of  $CO_2$ ,  $O_2$  and  $CO$  is taken as nitrogen.

**Precautions**

- The percentage of  $CO$  in the flue gas should be measured quite carefully since it is present to very small extent in the flue gas.
- In the beginning, the reagents in the absorption bulb 1, 2 and 3 should be brought to the etched mark levels one-by-one by operating the reservoir bottle and the valve of each bulb. Subsequently, these respective valves are closed.
- It is necessary to follow the order of absorbing the gases : First  $CO_2$ , second  $O_2$ , and last  $CO$ .
- Ensure a right volume of the flue gas is taken for analysis by strictly following the correct procedure discussed above.

**Notes :**

1. Potassium hydroxide solution for bulb 1 is made by dissolving 250 gm of  $KOH$  in 500 mL of freshly boiled distilled water. It absorbs  $CO_2$ .

2. Alkaline pyrogallol solution for bulb 2 is made by dissolving 25 gm pyrogallol acid and 200 gm  $KOH$  in 500 mL of distilled water. It absorbs  $O_2$ .

3. Ammonical cuprous chloride solution for bulb 3 is made by dissolving 100 gm cuprous chloride in a solution of 125 mL liquor ammonia plus 375 mL distilled water. It absorbs  $CO$ .

**Conversion of volumetric analysis to mass analysis of flue gases :**

As  $1\text{ m}^3$  of any gas = 1000 L of that gas

i.e.,  $1\text{ m}^3 = 1000\text{ L}$

Let total volume of the gas =  $V\text{ m}^3$  ; and molar mass of gas =  $M\text{ gm mol}^{-1}$

$$\Rightarrow V\text{ m}^3 = 1000\text{ V L}$$

$$= 1000\text{ V L} \times \frac{M\text{ gm}}{22.4\text{ L}} \quad [\because 1\text{ mol.} = 22.4\text{ L}]$$

$$= \left[ \frac{1000}{22.4} \times V \times M \right] \text{ gm}$$

S. No.	Gas	Volume (V) ( $\text{m}^3$ )	Mol. Mass (M)	Conversion of volume into mass	Percentage mass/kg of flue gas $\left( = \frac{V \times M}{T} \right) \times 100$
1.	G1	V1	M1	$\frac{1000}{22.4} (V_1 M_1)$	$\frac{V_1 M_1}{T} \times 100$
2.	G2	V2	M2	$\frac{1000}{22.4} (V_2 M_2)$	$\frac{V_2 M_2}{T} \times 100$
3.	G3	V3	M3	$\frac{1000}{22.4} (V_3 M_3)$	$\frac{V_3 M_3}{T} \times 100$
				Total = $(V_1 M_1 + V_2 M_2 + V_3 M_3)$ $\times \frac{1000}{22.4} = T \times \frac{1000}{22.4}$	



**Conversion of mass analysis to volume analysis of flue gases**

Suppose Amount (mass) of the gas =  $A$  gm

and molar mass of gas =  $M$  gm mol<sup>-1</sup>

$$\therefore \text{moles of the gas} = \frac{A}{M} \text{ moles}$$

As 1 mole of any gas occupies 22.4 litres of volume

i.e.,

$$1 \text{ mole} = 22.4 \text{ L}$$

$$= \frac{22.4}{1000} \text{ m}^3$$

$$[\because 1 \text{ m}^3 = 1000 \text{ L}]$$

$$\text{Now } \frac{A}{M} \text{ moles} = \frac{22.4}{1000} \times \frac{A}{M} \text{ m}^3$$

S. No.	Gas	Amount $A$ (gm)	Mol. mass $(M)$	Moles $= A/M$	Volume ( $\text{m}^3$ )	Percentage $\left( \frac{A/M}{T} \times 100 \right)$
1.	G1	$A_1$	$M_1$	$A_1/M_1$	$\frac{22.4}{1000} \times \frac{A_1}{M_1}$	$\frac{A_1/M_1}{T} \times 100$
2.	G2	$A_2$	$M_2$	$A_2/M_2$	$\frac{22.4}{1000} \times \frac{A_2}{M_2}$	$\frac{A_2/M_2}{T} \times 100$
					Total = $\frac{22.4}{1000} \left[ \frac{A_1}{M_1} + \frac{A_2}{M_2} \right]$ $= \frac{22.4}{1000} T$	

**13.1 Solved Numerical Examples based on Flue Gas Analysis**

**Example 1.** A coal sample gave the following analysis ;

$C = 66.2\%$  ;  $H = 4.2\%$  ;  $O = 6.1\%$  ;  $N = 1.4\%$  ;  $S = 2.9\%$  ; moisture =  $9.7\%$  and ash =  $9.5\%$ . If one kg of coal is burnt with 25% excess air, determine the quantity of products of combustion.

**Solution.** One kg of coal sample contains :

$$C = 662 \text{ gm} ; H_2 = 42 \text{ gm} ; S = 29 \text{ gm} ; O = 61 \text{ gm} ; H_2O = 97 \text{ gm}$$

Combustion reaction	Weight of oxygen needed for combustion	Weight of products of combustion
$C + O_2 \rightarrow CO_2$	$662 \times 32/12 = 1765.3 \text{ gm}$	$CO_2 = \frac{44}{12} \times 662 = 2427.3 \text{ gm}$
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	$42 \times 16/2 = 336 \text{ gm}$	$H_2O = 18/2 \times 42 = 378 \text{ gm}$
$S + O_2 \rightarrow SO_2$	$29 \times 32/32 = 29 \text{ gm}$	$SO_2 = 64/32 \times 29 = 58 \text{ gm}$
Total = 2130.3 gm		
Less $O_2$ in fuel = - 61 gm		
Net $O_2$ needed = 2069.3 gm		

As the air has 23% (by weight) oxygen,

Hence, minimum weight of air required for complete combustion of 1 kg of coal =  $2069.3 \times \frac{100}{23} = 8996.96 \text{ gm} = Z$  (let)

and weight of air supplied for combustion using 25% excess air

$$\begin{aligned} &= Z + Z \times \frac{25}{100} = Z \left( 1 + \frac{25}{100} \right) = Z \left( \frac{125}{100} \right) \\ &= 8996.96 \times \frac{125}{100} = 11246.2 \text{ gm} \end{aligned} \quad \dots(2)$$

Since, total weight of products of combustion

$$= \text{Weights of [excess } O_2 + N_2 + H_2O + SO_2 + CO_2] \quad \dots(3)$$

$\therefore$  We should first calculate the individual weights of products.

Now, weight of excess  $O_2 = 25\%$  of Net  $O_2$  used [equation (1)]

$$= 25/100 \times 2069.3 = 517.3 \text{ gm} \quad \dots(4)$$

Weight of  $N_2 = 77\%$  of weight of air + Weight of  $N_2$  present in fuel

$$= \frac{77}{100} \times 11246.2 + 14 = 8659.6 \text{ gm}$$

Weight of  $H_2O =$  Weight of  $H_2O$  formed from the combustion of  $H_2$

+ Weight of  $H_2O$  present in fuel.

$$= 378 + 97 = 475 \text{ gm ;}$$

Weight of  $SO_2 = 58 \text{ gm}$

Weight of  $CO_2 = 2427.3 \text{ gm}$

$\therefore$  Total weight of products of combustion

= weight of (excess  $O_2 + N_2 + H_2O + SO_2 + CO_2$ )

$$= 517.3 + 8659.6 + 475 + 58 + 2427.3 \text{ gm} = 12137.2 \text{ gm} = 12.137 \text{ kg}$$

**Example 2.** The composition by weight of a coal sample is : C = 80% ; H = 6% ; O = 8% ; S = 1% ; N = 2% and ash = 3%. Calculate : (i) minimum air required for complete combustion of 1.0 kg of coal ; (ii) the % composition of dry products of combustion of 1.0 kg of coal by weight. [RGPV, June 2002]

**Solution.** (i) 1 kg or 1000 gm of coal contains

$$C = 1000 \times 80/100 = 800 \text{ gm ; } H = 1000 \times 6/100 = 60 \text{ gm ;}$$

$$S = 1000 \times \frac{1}{100} = 10 \text{ gm ; } O = 1000 \times 8/100 = 80 \text{ gm ; and}$$

$$N = 1000 \times 2/100 = 20 \text{ gm}$$

Total weight of oxygen needed for combustion

$$\begin{aligned} &= \left( C \times \frac{32}{12} + H \times \frac{16}{2} + S \times \frac{32}{32} \right) \text{ gm} \\ &= \left( 800 \times \frac{32}{12} + 60 \times \frac{16}{2} + 10 \times \frac{32}{32} \right) \text{ gm} = 2623.3 \text{ gm} \end{aligned}$$

Less  $O_2$  in coal = 80 gm

$\therefore$  Net  $O_2$  needed for combustion =  $2623.3 - 80 = 2543.3 \text{ gm}$ . So, minimum weight of air necessary for complete combustion

$$= 2543.3 \times \frac{100}{23} = 11057.8 \text{ gm} = 11.058 \text{ kg.}$$

(ii) Dry products of combustion

$$\text{CO}_2 = \frac{44}{12} \times \text{C} = \frac{44}{12} \times 800 \text{ gm} = 2933.3 \text{ gm}$$

$$\text{SO}_2 = \frac{64}{32} \times \text{S} = \frac{64}{32} \times 10 \text{ gm} = 20 \text{ gm}$$

$$\text{N}_2 = 77\% \text{ of weight of air + in fuel}$$

$$= \frac{77}{100} \times 11057.8 + 20 = 8534.5 \text{ gm}$$

$$\text{Total weight of dry products of combustion} = \text{weight of } (\text{CO}_2 + \text{SO}_2 + \text{N}_2)$$

$$= 2933.3 + 20 + 8534.5 = 11487.8 \text{ gm}$$

$$\therefore \text{Percentage of CO}_2 = \frac{2933.3}{11487.8} \times 100 = 25.53\%$$

$$\text{Percentage of SO}_2 = \frac{20}{11487.8} \times 100 = 0.174\%$$

$$\text{and Percentage of N}_2 = \frac{8534.5}{11487.8} \times 100 = 74.29\%.$$

**Example 3.** The coal has the following analysis :

C = 54% ; H = 6.5% ; O = 3% ; N = 1.8 % moisture = 17.3 ; and remaining is ash.  
This coal, on combustion with excess of air, gave 21.5 kg of dry flue gases per kg of coal burnt. Calculate the percentage of excess air used for combustion.

**Solution.** 1 kg of coal contains :

$$\text{C} = 0.54 \text{ kg} ; \text{H} = 0.065 \text{ kg} ; \text{O} = 0.03 \text{ kg} ; \text{N} = 0.018 \text{ kg}$$

Minimum weight of air required for combustion

$$= \left( 0.54 \times \frac{32}{12} + 0.065 \times \frac{16}{2} - 0.03 \right) \times \frac{100}{23} = 8.39 \text{ kg}$$

Weight of dry products of combustion :

$$\text{CO}_2 = 0.54 \times 44/12 = 1.98 \text{ kg}$$

$$\text{N}_2 = 0.018 + 8.39 \times \frac{77}{100} = 6.478 \text{ kg}$$

$$\therefore \text{Total weight of dry products combustion} = 1.98 + 6.478 = 8.458 \text{ kg}$$

Given, the actual weight of dry flue gases is 21.5 kg, so balance must have come from excess air

$$= 21.5 - 8.458 = 13.042 \text{ kg.}$$

$$\text{Hence, percentage of excess air} = \frac{13.042}{8.39} \times 100 = 155.45\%$$

**Example 4.** A producer gas has the following composition by volume :  $\text{CH}_4 = 4.0\%$  ;  $\text{CO} = 26.0\%$  ;  $\text{H}_2 = 10.0\%$  ;  $\text{CO}_2 = 10.0\%$  and  $\text{N}_2 = 50\%$ .

Calculate : (i) minimum air required for complete combustion of  $1 \text{ m}^3$  of the fuel gas and (ii) % composition of dry products of combustion by volume, when 20% of excess air is used.  
[RGPV, Dec. 2002]



**Solution.** (i)  $1 \text{ m}^3$  of the producer gas contains :

$$\text{CH}_4 = 1 \times \frac{4}{100} = 0.04 \text{ m}^3 ; \text{CO} = 1 \times \frac{26}{100} = 0.26 \text{ m}^3 ;$$

$$\text{H}_2 = 1 \times \frac{10}{100} = 0.1 \text{ m}^3 ; \text{CO}_2 = 1 \times \frac{10}{100} = 0.1 \text{ m}^3 ; \text{ and}$$

$$\text{N}_2 = 1 \times \frac{50}{100} = 0.5 \text{ m}^3$$

Combustion equation	Volume of $\text{O}_2$ needed for combustion	Volume of dry products of combustion
$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$	$0.04 \text{ m}^3 \times 2 = 0.08 \text{ m}^3$	(i) $\text{CO}_2 = 0.04 \text{ m}^3 \times 1 = 0.04 \text{ m}^3$
$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	$0.26 \text{ m}^3 \times \frac{1}{2} = 0.13 \text{ m}^3$	$\text{CO}_2 = 0.26 \text{ m}^3 \times 1 = 0.26 \text{ m}^3$
$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$0.1 \text{ m}^3 \times \frac{1}{2} = 0.05 \text{ m}^3$	(plus $\text{CO}_2$ in producer gas = $0.1 \text{ m}^3$ )
	Total $\text{O}_2$ (y) = $0.26 \text{ m}^3$	$\therefore$ Total $\text{CO}_2 = 0.04 + 0.26 + 0.1 = 0.4 \text{ m}^3$
		(ii) $\text{N}_2 = 0.5 \text{ m}^3 + \frac{79}{100} z \times \frac{120}{100}$ $= 1.674 \text{ m}^3$
		(iii) $\text{O}_2$ (20% of y) = $y \times \frac{20}{100}$ $= 0.26 \times \frac{20}{100} = 0.052 \text{ m}^3$

Now, minimum air required for complete combustion of  $1 \text{ m}^3$  of the producer gas

$$(z) = y \times \frac{100}{21} = 1.238 \text{ m}^3.$$

(ii) Total volume of dry products of combustion

$$= \text{volume of } (\text{CO}_2 + \text{N}_2 + \text{O}_2)$$

$$= 0.4 + 1.674 + 0.052 = 2.126 \text{ m}^3$$

Now, % composition of dry products of combustion by volume is :

$$\text{CO}_2 = \frac{0.4}{2.126} \times 100 = 18.815\%$$

$$\text{N}_2 = \frac{1.674}{2.126} \times 100 = 78.739\%$$

$$\text{O}_2 = \frac{0.052}{2.126} \times 100 = 2.446\%.$$

**Example 5.** The percentage composition of a sample of coal by weight was found to be : C = 76% ; H = 5.2% ; O = 12.8% ; N = 2.7% ; S = 1.2%, the remaining being ash. Calculate the minimum : (a) weight, and (b) volume at NTP of air necessary for complete combustion of 1 kg of coal. Also calculate the percentage composition of dry products by weight, if 50% excess air is supplied.

**Solution.** 1 kg of coal contains

$$C = 760 \text{ gm} ; H = 52 \text{ gm} ; S = 12 \text{ gm} ; O = 128 \text{ gm} ; N = 27 \text{ gm}$$

$\therefore$  Net  $O_2$  needed for combustion =  $O_2$  needed for combustion -  $O_2$  in fuel

$$= \left( \frac{32}{12} \times 760 + \frac{16}{2} \times 52 + \frac{32}{32} \times 12 \right) - (128) = 2326.7 \text{ gm}$$

Now, weight of air necessary for complete combustion of 1 kg of coal

$$= 2326.7 \times \frac{100}{23} = 10115.9 \text{ gm} = 10.116 \text{ kg}$$

and, volume of air necessary for complete combustion of 1 kg of coal

$$= 10115.9 \text{ gm} \times \frac{22.4 \text{ L}}{28.94 \text{ gm}} \times \frac{1 \text{ m}^3}{1000 \text{ L}} = 7.83 \text{ m}^3$$

Weights and percentage of dry products of combustion are calculated below :

$$CO_2 = \frac{44}{12} \times 760 = 2786.7 \text{ gm}$$

$$SO_2 = \frac{64}{32} \times 12 = 24 \text{ gm}$$

$$N_2 = 27 \text{ gm (in fuel)} + \frac{77}{100} \times 10116 \times \frac{150}{100} = 11710.9 \text{ gm}$$

$$O_2 = \text{Minimum weight of } O_2 \times \frac{50}{100} = 2326.7 \times \frac{50}{100} = 1163.4 \text{ gm}$$

$$\begin{aligned} \text{Total weight of dry products of combustion} &= \text{weight of } (CO_2 + SO_2 + N_2 + O_2) \\ &= 2786.7 + 24 + 11710.9 + 1163.4 = 15684.97 \text{ gm} \end{aligned}$$

$$\therefore \text{Percentage of } CO_2 = \frac{2786.7}{15684.97} \times 100 = 17.77\%$$

$$\text{Percentage of } SO_2 = \frac{24}{15684.97} \times 100 = 0.153\%$$

$$\text{Percentage of } N_2 = \frac{11710.9}{15684.97} \times 100 = 74.7\%$$

$$\text{Percentage of } O_2 = \frac{1163.4}{15684.97} \times 100 = 7.417\%$$

**Example 6.** The percentage composition of a sample of bituminous coal was found to be as under :  $C = 75.4$ ,  $H = 4.5$ ,  $O = 12.5$ ,  $N = 3.1$ ,  $S = 1.4$ .

The rest being ash, calculate the minimum weight of air necessary for complete combustion of 1 kg of coal and percentage composition of the dry products of combustion by weight.

[MREC 2000]

**Solution.** (i) 1 kg of bituminous coal contains :

$$C = 754 \text{ gm}, H = 45 \text{ gm}, S = 14 \text{ gm}, O = 125 \text{ gm and } N = 31 \text{ gm.}$$

$$\text{Net } O_2 = \left[ \frac{32}{12} \times 754 + \frac{16}{2} \times 45 + \frac{32}{32} \times 14 \right] - 125 = 2259.7 \text{ gm}$$

$$\therefore \text{Minimum air required} = \text{Net } O_2 \times \frac{100}{23} = 9824.6 \text{ gm.}$$

(ii)

Dry Products	Amounts	Percentage Composition
CO <sub>2</sub>	$\frac{44}{12} \times 754 = 2764.7 \text{ gm}$	$\frac{2764.7}{10388.6} \times 100 = 26.6\%$
N <sub>2</sub>	$31 \text{ gm in fuel} + \frac{77}{100} \times 9824.6 = 7595.9 \text{ gm}$	$\frac{7595.9}{10388.6} \times 100 = 73.1\%$
SO <sub>2</sub>	$\frac{64}{32} \times 14 = 28 \text{ gm}$	$\frac{28}{10388.6} \times 100 = 0.27\%$
Total weight of Dry Products = $2764.7 + 7595.9 + 28 = 10388.6 \text{ gm}$ .		

**Example 7.** The percentage composition by weight of a sample of coal was found to be as under :

C = 81%, H = 5%, O = 8.5%, S = 1%, N = 1% and ash = 3.5%.

(i) Calculate the minimum amount of O<sub>2</sub> and air required for complete combustion of 1 kg of this coal.

(ii) Percentage composition by weight of the dry products of combustion.

[Raj. Univ. 2002]

**Solution.** (i) 1 kg of coal contains :

C = 810 gm, H = 50 gm, S = 10 gm, O = 85 gm, N = 10 gm.

$$\therefore \text{Net O}_2 = \left[ \frac{32}{12} \times 810 + \frac{16}{2} \times 50 + \frac{32}{32} \times 10 \right] - 85 = 2485 \text{ gm}.$$

$$\text{And minimum amount of air} = \text{Net O}_2 \times \frac{100}{23} = 10804.35 \text{ gm} = 10.8 \text{ kg}.$$

(ii)

Dry Products	Amounts	Percentage Composition
CO <sub>2</sub>	$\frac{44}{12} \times 810 = 2970 \text{ gm}$	$\frac{2970}{11319.4} \times 100 = 26.2\%$
SO <sub>2</sub>	$\frac{64}{32} \times 10 = 20 \text{ gm}$	$\frac{20}{11319.4} \times 100 = 0.177\%$
N <sub>2</sub>	$10 \text{ gm in fuel} + \frac{77}{100} \times 10804.35 = 8329.4 \text{ gm}$	$\frac{8329.4}{11319.4} \times 100 = 73.6\%$
Total weight of dry products = $2970 + 20 + 8329.4 = 11319.4 \text{ gm}$ .		

**Example 8.** A boiler is fired with a coal having the following percentage composition :

C = 75%, H = 9%, S = 2%, O = 4%, N = 3%, Ash = 7%

Calculate : (i) Gross and net calorific value of 1 kg of coal, (ii) Minimum theoretical air required for combustion of 1 kg of coal (by weight) (iii) Percentage composition of dry flue gas if 25% excess air is used. [RGPV, Dec. 2003]

**Solution.** (i) Gross calorific value (GCV)

$$= \frac{1}{100} \left[ 8080 C + 34500 \left( H - \frac{O}{8} \right) + 2240 S \right] \text{ cal/gm}$$



Net calorific value (NCV) =  $[GCV - 0.09 H \times 587]$  cal/gm  
 where C, H, O and S are the % of carbon, hydrogen, oxygen and sulphur.

$$\therefore GCV = \frac{1}{100} \left[ 8080 \times 75 + 34500 \left( 9 - \frac{4}{8} \right) + 2240 \times 2 \right] \text{ cal/gm}$$

$$= 9037.3 \text{ cal/gm.}$$

$$NCV = [9037.3 - 0.09 \times 9 \times 587] \text{ cal/gm} = 8561.8 \text{ cal/gm}$$

(ii) 1 kg or 1000 gm of coal contains :

$$C = 1000 \times \frac{75}{100} = 750 \text{ gm} ; H = 1000 \times \frac{9}{100} = 90 \text{ gm} ;$$

$$S = 1000 \times \frac{2}{100} = 20 \text{ gm} ; O = 1000 \times \frac{4}{100} = 40 \text{ gm} ;$$

and

$$N = 1000 \times \frac{3}{100} = 30 \text{ gm.}$$

Combustion reaction	Weight of O <sub>2</sub> required for combustion	Weight of dry products of combustion
$\begin{array}{ccc} C + O_2 & \rightarrow & CO_2 \\ 12 & 32 & 44 \end{array}$	$750 \times \frac{32}{12} = 2000 \text{ gm}$	(i) $CO_2 = 750 \times \frac{44}{12} = 2750 \text{ gm}$
$\begin{array}{ccc} H_2 + \frac{1}{2} O_2 & \rightarrow & H_2O \\ 2 & 16 & 18 \end{array}$	$90 \times \frac{16}{2} = 720 \text{ gm}$	
$\begin{array}{ccc} S + O_2 & \rightarrow & SO_2 \\ 32 & 32 & 64 \end{array}$	$20 \times \frac{32}{32} = 20 \text{ gm}$	(ii) $SO_2 = 20 \times \frac{64}{32} = 40 \text{ gm}$
	Total O <sub>2</sub> = 2740 gm	(iii) $N_2 = 30 \text{ gm in fuel} + \frac{77}{100} \times 11739.13 \times \frac{125}{100} = 11328.9 \text{ gm}$
	Less O <sub>2</sub> in fuel = 40 gm $\therefore$ Net O <sub>2</sub> needed = $2740 - 40 = y = 2700 \text{ gm}$	(iv) O <sub>2</sub> [25% of net O <sub>2</sub> (y)] $= y \times \frac{25}{100} = 2700 \times \frac{25}{100} = 675 \text{ gm}$

(ii) Now, minimum theoretical air required for combustion of 1 kg of coal (by weight)

$$= 2700 \times \frac{100}{23} = 11739.13 \text{ gm}$$

(iii) Total weight of dry flue gases

$$= \text{weights of } (CO_2 + SO_2 + N_2 + \text{excess } O_2)$$

$$= 2750 + 40 + 11328.9 + 675 = 14793.9 \text{ gm}$$

$\therefore$  Percentage composition of dry flue gases

$$CO_2 = \frac{2750}{14793.9} \times 100 = 18.6\% ; SO_2 = \frac{40}{14793.9} \times 100 = 0.3\%$$

$$N_2 = \frac{11328.9}{14793.9} \times 100 = 76.6\% ; O_2 = \frac{675}{14793.9} \times 100 = 4.6\%$$

**Example 9.** The % composition by weight of a sample of coal was found to be as :

Constituent	C	H <sub>2</sub>	O <sub>2</sub>	S	Moisture	N <sub>2</sub>	Ash
%	90	3.5	3	0.5	1	0.5	1.5

Calculate (a) The minimum weight of air required for the complete combustion of 1 kg of coal ;

(b) The volume at NTP of air required for the complete combustion of 1 kg of coal,

(c) The % composition by (i) weight and (ii) volume of the dry products of combustion (ash not included).

**Solution.** (a) Total weight of O<sub>2</sub> needed

$$= \left( C \times \frac{32}{12} + H_2 \times \frac{16}{2} + S \times \frac{32}{32} \right) \text{ gm}$$

$$= \left( 900 \times \frac{32}{12} + 35 \times \frac{16}{2} + 5 \times \frac{32}{32} \right) = 2685 \text{ gm}$$

Less O<sub>2</sub> is coal = 30 gm

∴ Net O<sub>2</sub> needed for combustion of 1 kg of Coal = 2685 – 30 = 2655 gm

Now, the minimum weight of air necessary for complete combustion of 1 kg of coal

$$= 2655 \times \frac{100}{23} = 11543.48 \text{ gm} \approx 11.54 \text{ kg} \quad \dots(i)$$

(b) As 1 mole (= 32 g) of O<sub>2</sub> occupies = 22.4 L volume at NTP or 32 kg of O<sub>2</sub> occupies 22.4 m<sup>3</sup> at NTP

$$1 \text{ kg of O}_2 \text{ occupies} = \frac{22.4}{32} \text{ m}^3$$

$$2.655 \text{ kg of O}_2 \text{ occupies} \frac{22.4}{32} \times 2.655 = 1.8585 \text{ m}^3 \text{ at NTP.}$$

As 21 m<sup>3</sup> of O<sub>2</sub> are present in 100 m<sup>3</sup> of air at NTP

$$\therefore 1.8585 \text{ m}^3 \text{ of O}_2 \text{ are present in} \left( \frac{100}{21} \times 1.8585 = 8.85 \text{ m}^3 \right) \text{ of air at NTP.}$$

Thus, volume of air at NTP = 8.85 m<sup>3</sup> ...(ii)

(c) (i) Weight and % of dry products of combustion are calculated below :

$$\text{Weight of CO}_2 = \frac{44}{12} \times 900 = 3300 \text{ gm} = 3.30 \text{ kg}$$

$$\text{Weight of SO}_2 = \frac{64}{32} \times 5 = 10 \text{ gm} = 0.01 \text{ kg}$$

$$\text{Weight of N}_2 = 5 \text{ gm in fuel} + \frac{77}{100} \times 11543.5 = 8893.5 \text{ gm} = 8.89 \text{ kg}$$

$$\text{Total weight of combustion products} = 3.30 + 0.01 + 8.89 = 12.2 \text{ kg}$$

$$\therefore \text{Weight \% of CO}_2 = \frac{3.30}{12.2} \times 100 = 27$$

$$\text{Weight \% of SO}_2 = \frac{0.01}{12.2} \times 100 = 8.2 \times 10^{-4} = 0.082 \quad \dots(iii)$$

$$\text{Weight \% of N}_2 = \frac{8.89}{12.2} \times 100 = 0.7287 = 72.8$$

(ii) Volume and % of dry products of combustion are calculated below :

$$\text{Volume of CO}_2 = \left( \frac{3.30 \text{ kg}}{44 \text{ kg/k mol}} \right) \times \left( \frac{22.4 \text{ m}^3}{1 \text{ K mol}} \right) = 0.075 \times 22.4 \text{ m}^3$$

$$\text{Volume of SO}_2 = \left( \frac{0.01 \text{ kg}}{64 \text{ kg/k mol}} \right) \times \left( \frac{22.4 \text{ m}^3}{1 \text{ k mol}} \right) = 0.00016 \times 22.4 \text{ m}^3$$

$$\text{Volume of N}_2 = \left( \frac{8.89 \text{ kg}}{28 \text{ kg/k mol}} \right) \times \left( \frac{22.4 \text{ m}^3}{1 \text{ k mol}} \right) = 0.3175 \times 22.4 \text{ m}^3$$

$$\therefore \text{Total volume of dry products of combustion} = 0.3927 \times 22.4 \text{ m}^3$$

$$\text{Thus, volume \% of CO}_2 = \frac{0.075}{0.3927} \times 100 = 19.09$$

$$\text{Volume \% of SO}_2 = \frac{0.00016}{0.3927} \times 100 = 0.41 \quad \dots(iv)$$

$$\text{Volume \% of N}_2 = \frac{0.3175}{0.3927} \times 100 = 80.85$$

**Example 10.** 100 kg of a liquid hydrocarbon fuel containing 89.4 %C by weight is burnt with (i) theoretical amount of air (ii) 20% excess of the theoretically required amount of air. Calculate the volumetric composition of products in each case.

**Solution.** 100 kg of a liquid hydrocarbon fuel containing

$$C = 89.4 \text{ kg} = \frac{89.4}{12} = 7.45 \text{ k mol and } H = 100 - 89.4 = 10.6 \text{ kg} = \frac{10.6}{2} = 5.3 \text{ k mol.}$$

Combustion Equation	Kilomoles of O <sub>2</sub>	Kilomoles of Products formed
$C + O_2 \rightarrow CO_2$	$7.45 \times 1 = 7.45$	7.45 (CO <sub>2</sub> )
$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$5.3 \times \frac{1}{2} = 2.65$	5.3 (H <sub>2</sub> O)

$$\text{Total O}_2 \text{ required} = 7.45 + 2.65 = 10.1 \text{ k mol.}$$

(i) Theoretical amount of air required for combustion

$$= 10.1 \times \frac{100}{21} = 48.1 \text{ k mol}$$

$$\text{Amount of N}_2 \text{ present in flue gases} = 48.1 \times \frac{79}{100} = 38 \text{ k mol}$$



The composition of the flue gas is given below :

$$\text{CO}_2 = 7.45 \text{ k mol}$$

$$\text{H}_2\text{O (vapour)} = 5.3 \text{ k mol}$$

$$\text{N}_2 = 38 \text{ k mol}$$

$$\text{Total} = \underline{50.75 \text{ k mol.}}$$

As 1 k mol of any gas at NTP occupies  $22.4 \text{ m}^3$ , the volume % composition (by volume) of the flue gas is :

$$\% \text{ of CO}_2 = \frac{7.45}{50.75} \times 100 = 14.679$$

$$\% \text{ of H}_2\text{O} = \frac{5.3}{50.75} \times 100 = 10.443$$

$$\% \text{ of N}_2 = \frac{38}{50.75} \times 100 = 74.876$$

(ii) When 20% excess air is used

$$\text{Quantity of air required} = 48.1 \times \frac{120}{100} = 57.72 \text{ k mol.}$$

Now, the flue gas will also contain excess  $\text{O}_2$  (i.e.,  $\text{O}_2$  not used for combustion).

$$\text{Amount of nitrogen present} = 57.72 \times \frac{79}{100} = 45.6 \text{ k mol.}$$

$$\text{Amount of oxygen present in this air} = 57.72 - 45.6 = 12.12 \text{ k mol.}$$

As 10.1 k mol of  $\text{O}_2$  is required for combustion. Thus, amount of  $\text{O}_2$  in the flue gas =  $12.12 - 10.1 = 2.02 \text{ k mol.}$

Thus, the composition of the flue gas is given below :

$$\text{CO}_2 = 7.45 \text{ k mol}$$

$$\text{H}_2 \text{ vapour} = 5.3 \text{ k mol}$$

$$\text{N}_2 = 45.6 \text{ k mol}$$

$$\text{O}_2 = 2.02 \text{ k mol}$$

$$\text{Total} = \underline{60.37 \text{ k mol.}}$$

Now, the % composition (by volume) of the flue gas is :

$$\% \text{ CO}_2 = \frac{7.45}{60.37} \times 100 = 12.34$$

$$\% \text{ H}_2\text{O} = \frac{5.3}{60.37} \times 100 = 8.779$$

$$\% \text{ N}_2 = \frac{45.6}{60.37} \times 100 = 75.534$$

$$\% \text{ O}_2 = \frac{2.02}{60.37} \times 100 = 3.346$$

**Example 11.** A sample of coal having the following percentage composition by weight :

Constituent	C	H	O	S	Moisture	Ash
%	88	4	5	1	1	1

It was used as a boiler fuel and the flue gas had the following % composition by volume.

Gas	CO <sub>2</sub>	CO	O <sub>2</sub>	SO <sub>2</sub>	N <sub>2</sub>
%	11	1.5	7	0.5	80

Find (i) Weight of air required for the complete combustion of 1 kg of coal ; (ii) Weight of flue gases per kg of fuel burnt ; (iii) Percentage of air used in excess ; and (iv) Percentage of carbon burned to CO.

**Solution.** (i) 1 kg of coal contain

$$C = 0.88 \text{ kg} = \frac{0.88}{12} = 0.073 \text{ k mol ;}$$

$$H = 0.04 \text{ kg} = \frac{0.04}{2} = 0.02 \text{ k mol ;}$$

$$O = 0.05 \text{ kg} = \frac{0.05}{32} = 1.563 \times 10^{-3} \text{ k mol ;}$$

$$S = 0.01 \text{ kg} = \frac{0.01}{32} = 3.125 \times 10^{-4} \text{ k mol.}$$

Combustion Equation	Kilo moles of O <sub>2</sub> needed	Kilo moles of Products formed
C + O <sub>2</sub> → CO <sub>2</sub>	0.073 × 1 = 0.073	0.073 (CO <sub>2</sub> )
H <sub>2</sub> + $\frac{1}{2}$ O <sub>2</sub> → H <sub>2</sub> O	0.02 × $\frac{1}{2}$ = 0.01	0.01 (H <sub>2</sub> O)
S + O <sub>2</sub> → SO <sub>2</sub>	3.125 × 10 <sup>-4</sup> × 1 = 3.125 × 10 <sup>-4</sup>	3.125 × 10 <sup>-4</sup> (SO <sub>2</sub> )
	Total = 0.0833	
	Less in Fuel = - 1.563 × 10 <sup>-3</sup>	
	Net = 0.08175 k mol.	

$$\text{Weight of O}_2 \text{ needed} = 0.08175 \text{ k mol} \times \frac{32 \text{ kg}}{1 \text{ k mol}} = 2.616 \text{ kg}$$

$$\therefore \text{Weight of air required for complete combustion of 1 kg of coal} \\ = 2.616 \times \frac{100}{23} = 11.37 \text{ kg.} \quad \dots(a)$$

**Alternative.**

1 kg of coal contains : C = 880 gm, H = 40 gm, S = 10 gm, O = 50 gm.

(i) Theoretical weight of air required for complete combustion of 1 kg of coal

$$= \left[ 880 \times \left( \frac{32}{12} \right) + 40 \times \left( \frac{16}{2} \right) + 10 \times \left( \frac{32}{32} \right) - 50 \right] \times \frac{100}{23} = 11420 \text{ gm} \\ = 11.4 \text{ kg} \quad \dots(a)$$

(ii) 1 m<sup>3</sup> of flue gas contains : CO<sub>2</sub> = 0.11 m<sup>3</sup> ; CO = 0.015 m<sup>3</sup> ; O<sub>2</sub> = 0.07 m<sup>3</sup> , SO<sub>2</sub> = 0.005 m<sup>3</sup> and N<sub>2</sub> = 0.8 m<sup>3</sup>

Conversion of volumetric analysis to mass analysis :

Flue gas	Volume (V) (in m <sup>3</sup> )	Mol. mass (M)	V × M Product	Mass/kg of flue gas
CO <sub>2</sub>	0.11	44	4.84	4.84/30.22 = 0.16 kg
CO	0.015	28	0.42	0.42/30.22 = 0.0139 kg
O <sub>2</sub>	0.07	32	2.24	2.24/30.22 = 0.074 kg
SO <sub>2</sub>	0.005	64	0.32	0.32/30.22 = 0.0106 kg
N <sub>2</sub>	0.8	28	22.4	22.4/30.22 = 0.74 kg
			Total = 30.22	Total = 0.9985 = 1 kg

Weight of flue gas/kg of coal burnt

$$\frac{\text{Weight of C/kg of coal (Let } a)}{\text{Weight of C/kg of flue gas (Let } b)}$$

$$\begin{aligned} \text{Now weight of C/kg of flue gas} &= \text{Weight of CO}_2 \times \frac{12}{44} + \text{weight of CO} \times \frac{2}{28} \\ &= 0.16 \times \frac{12}{44} + 0.0139 \times \frac{12}{28} = 0.0496 \text{ kg (= } b). \end{aligned}$$

Given, weight of C/kg of coal = 0.880 kg (= a)

$$\text{Thus, weight of flue gas/kg of coal burnt} = \frac{0.880}{0.049} = 17.7 \text{ kg.}$$

As 1 kg of coal also contains 1 % moisture (i.e., H<sub>2</sub>O = 0.01 kg) and 4% hydrogen ; which will form H<sub>2</sub>O =  $\frac{18}{2} \times 0.04 = 0.36$  kg.

Thus, weight of water present in 1 kg of the gas = 0.01 + 0.36 = 0.37 kg

Thus, weight of flue gas (including moisture) per kg of fuel burnt = 17.7 + 0.37 = 18.07 kg ... (b)

(iii) Percentage of excess air supplied for combustion

$$= \frac{\text{Excess air}}{\text{Theoretical air}} \times 100 \quad \dots (c)$$

from Answer of Part (i), Theoretical air = 11.4 kg. ... (a)

$$\text{Now Excess air/kg of coal burnt} = \frac{100}{23} \times (\text{Excess O}_2/\text{kg of coal burnt}) \quad \dots (d)$$

$$\text{And excess O}_2/\text{kg of coal burnt} = \left( \frac{\text{excess O}_2}{\text{kg of flue gas}} \right) \times \left( \frac{\text{mass of flue gas}}{\text{kg of coal burnt}} \right) \quad \dots (e)$$

From answer of Part (ii), weight of flue gas per kg of coal burnt = 18.07 kg, ... (b)

Now, weight of excess O<sub>2</sub> per kg of flue gas

= Mass of O<sub>2</sub> (in flue gas – required to convert 0.0139 kg CO to CO<sub>2</sub>)

$$= 0.074 - \left( \frac{16}{28} \right) \times 0.0139 = 0.066 \text{ kg} \quad \dots (f)$$



Substituting the results (b) and (f) in equation (e), we get

$$\text{Excess O}_2/\text{kg of coal burnt} = (0.066) \times (18.07) = 1.193 \quad \dots(g)$$

Substituting (g) in (d), we get

$$\text{Excess air/kg of coal burnt} = \frac{100}{23} \times 1.193 = 5.187 \quad \dots(h)$$

Substituting the results (h) and (a) in eqn. (c), we get

$$\text{Percentage of excess air supplied for combustion} = \frac{5.187}{11.4} \times 100 = 45.5 \quad \dots(i)$$

$$(iv) \% \text{ of C burned to CO} = \frac{\text{Wt. of C as CO in flue gas}}{\text{Total wt. of C in the flue gas}} \times 100$$

$$= \left( \frac{0.0139 \times \frac{12}{28}}{0.0139 \times \frac{12}{28} + 0.16 \times \frac{12}{44}} \right) \times 100 = 12. \quad \dots(j)$$

**Example 12.** A hydrocarbon fuel on combustion gave a flue gas of the following volume % composition :  $\text{CO}_2 = 13.53$ ,  $\text{N}_2 = 82.91$  and  $\text{O}_2 = 3.56$ . Determine composition of fuel by weight ; (b) the % of air used in excess, and (c) volume of air supplied per kg of the fuel.

**Solution.** (a) As the flue gas contains  $\text{CO}_2$  so one of the constituent in fuel must be carbon.

Moreover, combustion reaction for carbon is :  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$

This indicates that moles of  $\text{CO}_2$  = moles of  $\text{O}_2$  = moles of C.

Assuming total amount of dry flue gas = 100 k mol, so moles of  $\text{CO}_2 = 13.53$  k mol

Thus, amount of  $\text{O}_2$  in flue gas

$$= 13.53 \text{ (from CO}_2\text{)} + 3.56 \text{ (from free O}_2\text{ in flue gas)}$$

$$= 17.09 \text{ k mol}$$

..(i)

Given amount of  $\text{N}_2$  in the flue gas = 82.91 k mol.

We know that, In 100 k mol air, 79 k mol  $\text{N}_2$  is present (i.e., 79%  $\text{N}_2$  by volume)

Thus, amount of air supplied for combustion

$$= \frac{100}{79} \times 82.91 \text{ k mol} = 104.95 \text{ k mol} \quad \dots(iia)$$

$$\therefore \text{Amount of O}_2 \text{ supplied} = 104.95 \times \frac{21}{100} = 22.039 = 22.04 \text{ k mol} \quad \dots(iib)$$

From (i) and (iib), it can be concluded that,

Amount of  $\text{O}_2$  that has combined with  $\text{H}_2 = 22.04 - 17.09 = 4.95$  k mol

The combustion equation for  $\text{H}_2$  is :  $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$

so Amount of  $\text{H}_2$  burnt =  $2 \times 4.95 = 9.90$  k mol.

$$\text{And weight of H}_2 \text{ burnt} = 9.9 \times 2 = 19.8 \text{ kg.} \quad \dots(iii)$$

As 100 k mol of flue gas containing 13.53 k mol of  $\text{CO}_2$  or 13.53 k mol of C.

$\therefore$  Amount of C in the fuel = 13.53 k mol

$\Rightarrow$  Weight of C in the fuel =  $13.53 \times 12 = 162.36$  kg. ... (iv)

$$\text{Now } \%C = \frac{162.36}{162.36 + 19.80} \times 100 = 89.130$$

$$\%H = \frac{19.80}{162.36 + 19.80} \times 100 = 10.869 = 10.87 \quad \dots (v)$$

(b) Theoretically, amount of  $\text{O}_2$  required for producing 13.53 k moles of  $\text{CO}_2 = 13.53$  k moles.

Moreover, amount of  $\text{O}_2$  required for burning  $\text{H}_2 = 4.95$  k moles

Thus, total amount of  $\text{O}_2$  theoretically required =  $13.53 + 4.95 = 18.48$  k moles

From (ii), Amount of  $\text{O}_2$  supplied = 22.04 k moles

$$\text{so, \% of excess air} = \frac{22.04 - 18.48}{18.48} \times 100 = 19.264 \quad \dots (vi)$$

(c) From (iii) and (iv)

Total weight of hydrocarbon fuel undergoing combustion

$$= 162.36 + 19.8 = 182.16 \text{ kg} \quad \dots (vii)$$

Moreover, from equation (iia),

Total air supplied = 104.95 k mol

$$= 104.95 \times 22.4 = 2350.93 \text{ m}^3 \quad \dots (viii)$$

Thus, volume of air supplied per kg of the fuel

$$= \frac{2350.93 \text{ m}^3}{182.16 \text{ kg}} = 12.91 \text{ m}^3/\text{kg}. \quad \dots (ix)$$

**Example 13.** A fuel contained only C (90% by weight) and H (6% by weight). It was burnt in 90% of air of that required for complete combustion. Find out the % composition of dry products of combustion by mass, if H is burnt completely and no carbon is left behind.

**Solution.** Let Amount of fuel taken = 1000 gm

$$\therefore \text{Amount of C in fuel} = 1000 \times \frac{90}{100} = 900 \text{ gm}$$

and  $\text{Amount of H in fuel} = 1000 \times \frac{6}{100} = 60 \text{ gm}$

Constituent	Amount (gm)	Combustion reaction	Weight of $\text{O}_2$ required (gm)
C	900	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$900 \times \frac{32}{12} = 2400$
H	60	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$60 \times \frac{16}{2} = 480$
			Total = 2880 gm

Theoretical air required for complete combustion of 1 kg of fuel

$$= 2880 \times \frac{100}{23} = 12521.7 \text{ gm}$$

$$\therefore \text{Weight of air actually used} = 12521.7 \times \frac{90}{100} = 11269.5 \text{ gm} \quad \dots(i)$$

It is given that insufficient air is used and H is burnt completely. This indicates part of C is oxidised to  $\text{CO}_2$  and remaining C is oxidised to CO.

Let  $x$  gm of C is oxidised to CO, so  $(900 - x)$  gm of C is oxidised to  $\text{CO}_2$ .

Constituent	Amount (gm)	Combustion reaction	Weight of $\text{O}_2$ required (gm)
C	$x$ (let)	$\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}$	$x \times \frac{16}{12} = \frac{16}{12} x$
C	$90 - x$	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$(900 - x) \times \frac{32}{12} = 2400 - \frac{32}{12} x$
H	60	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$60 \times \frac{16}{2} = 480$
Total			$= 2880 - 1.33 x$

$$\therefore \text{Air requirement} = (2880 - 1.33x) \times \frac{100}{23} = 12521.7 - 5.783 x \quad \dots(ii)$$

But from (i), weight of air actually used = 11269.5 gm

$$\therefore 11269.5 = 12521.7 - 5.783 x$$

$$\Rightarrow x = 216.5 \text{ gm}$$

$\therefore$  Weight of C oxidised to CO = 216.5 gm

and weight of C oxidised to  $\text{CO}_2 = 900 - 216.5 = 683.5 \text{ gm} \quad \dots(iii)$

Calculation of weight of dry products of combustion per kg of fuel :

$$\text{Weight of CO} = 216.5 \times \frac{28}{12} = 505.2 \text{ gm}$$

$$\text{Weight of CO}_2 = 683.5 \times \frac{44}{12} = 2506.2 \text{ gm}$$

$\dots(iv)$

$$\text{Weight of N}_2 \text{ (air used)} = 11269.5 \times \frac{77}{100} = 8677.5 \text{ gm}$$

$$\begin{aligned} \text{Total weight of dry product of combustion} &= 505.2 + 2506.2 + 8677.5 \\ &= 11688.9 \text{ gm} \end{aligned}$$

Calculation of the % composition of dry products of combustion

$$\text{CO} = \frac{505.2}{11688.9} \times 100 = 4.32\%$$

$$\text{CO}_2 = \frac{2506.2}{11688.9} \times 100 = 21.44\%$$

$$\text{N}_2 = \frac{8677.5}{11688.9} \times 100 = 74.2\%$$

$\dots(v)$



## 14 PETROLEUM

Petroleum or crude oil is a source of many liquid fuels that are in current use. The word petroleum is derived from latin, (Petra = rock ; oleum = oil). Petroleum is also called mineral oil because it occurs beneath the earth.

The composition (average) of petroleum is as follows :

(C = 80 to 87%) ; (H = 11.1 to 15%) ; (S = 0.1 to 3.5%) ;

(O = 0.1 to 0.9%) and (N = 0.4 to 0.9%).

**Petroleum** is a complex mixture of paraffinic, olefinic and aromatic hydrocarbons with small quantities of organic compounds containing oxygen, nitrogen and sulphur. The common constituents present in petroleum are summarized in Table 7 below :

**Table 7. Constituents of Petroleum**

Constituent	Remarks
Hydrocarbons	These are present to the extent of 70%. Apart from normal, branched and cycloalkanes, lower boiling fractions also contain alkyl benzenes. Higher boiling fractions contain polynuclear aromatics like naphthalenes. Terpenes are also present to small extent.
Sulphur containing compounds	Sulphur is also present either in elemental form or in the form of inorganic/organic sulphur compounds, viz. H <sub>2</sub> S. Thiols, Thiophene, thioalkanes etc.
Oxygen containing compounds	(C <sub>4</sub> – C <sub>9</sub> ) carboxylic acids occur in low boiling fractions while naphthenic acids occur in high-boiling fractions. Trace amounts of phenols and cresols also present.
Nitrogen containing compounds	These are present in traces and are mainly pyrrole, indole, pyridine, quinoline etc.
Inorganic compounds	These are organometallic compounds of Cu, Fe, Ni and V to very little extent.

### 14.1 Origin of Petroleum

Following two theories are proposed on the origin of petroleum :

(i) **Carbide theory.** It postulates that metal carbides are formed under the earth's crust due to the interaction of metals and carbon under high temperature and pressure. These carbides react with steam or water giving lower hydrocarbons, which further undergo hydrogenation and polymerization and eventually generate a complex mixture of paraffinic, olefinic and aromatic hydrocarbons.

**Pros :** This theory is mainly based on laboratory experiments, (ii) This theory is further reinforced by the claim of Moison that by the action of steam on uranium carbide, a liquid resembling crude oil is obtained.

**Cons :** Carbide theory fails to explain the presence of sulphur, nitrogen, chlorophyll, porphyrin and optically active compounds in the petroleum.

(ii) **Organic or modern theory.** According to this theory, petroleum has formed from the partial decomposition of marine animals and vegetable organisms of pre-historic forests. Volcano's, earth movements, etc. had buried these materials underground, where they have been subjected to intense heat and pressure for very long time. The conversion of these materials into various hydrocarbons has been going on either by

- (a) the bacterial decomposition under anaerobic and strongly reducing conditions and temperature under high pressure, or by
- (b) under the influence of radioactive substances like uranium.

#### 14.2 Mining of Petroleum

This is done by drilling holes in the earth's crust and sinking pipes upto the oil-bearing porous rocks. Oil usually rushes out to the surface by itself because of the hydrostatic pressure of the natural gas. Later, when the pressure becomes too low, it may have to be mechanically pumped up with the help of lift pumps.

The air-lift pumps comprise of two co-axial pipes which are sunk into the oil bed and compressed air is forced through the outer-pipe, whereby oil comes out through the inner pipe (Fig. 15). The oil is then conveyed to refinery for refining.

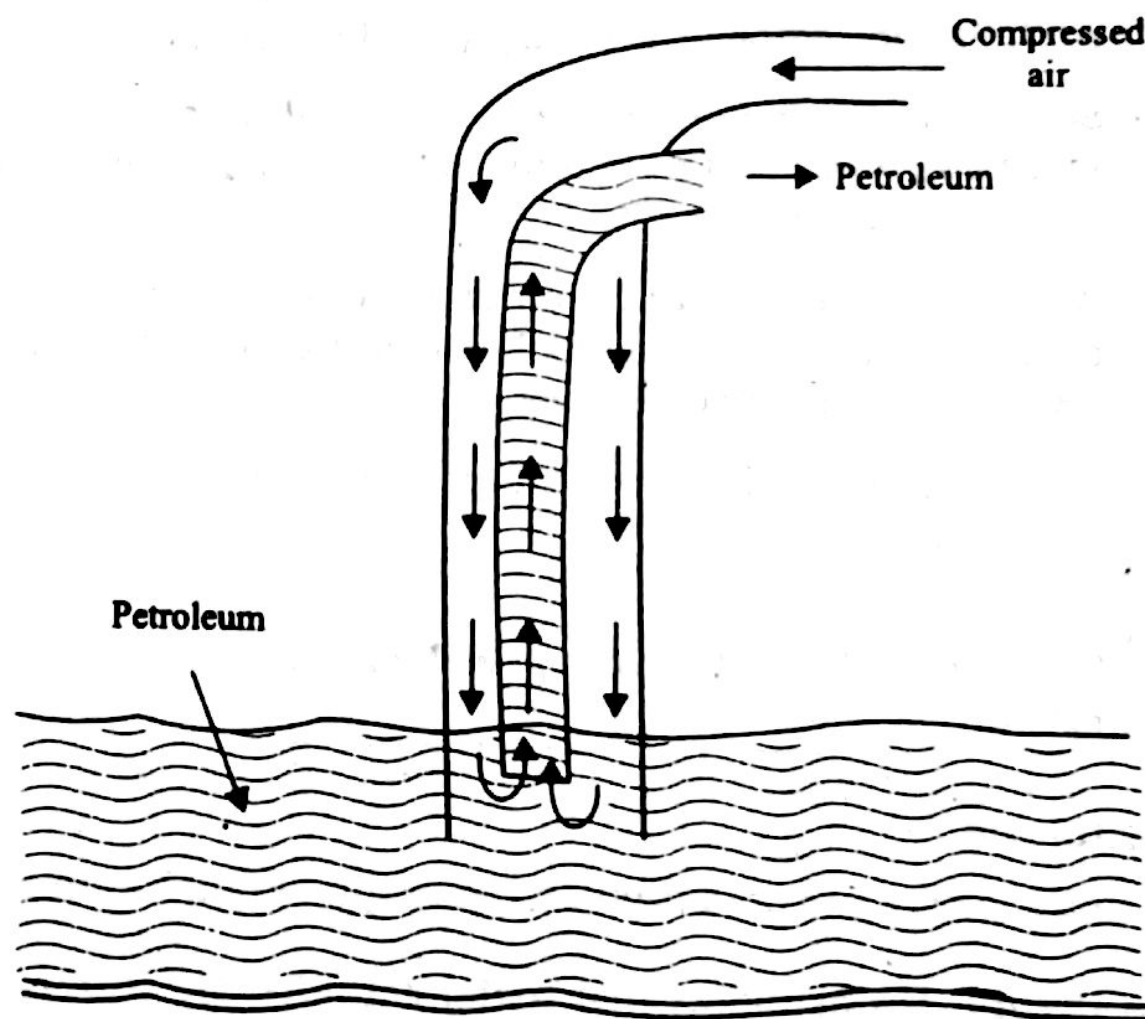


Fig. 15. Mechanical pumping of petroleum by using air-lift pump.

#### 14.3 Classification of Petroleum

The chemical nature of the crude petroleum varies with the part of the world in which it is found. There are three main types of crude oil :

(i) **Paraffinic base type crude oil.** They mainly consist of the saturated hydrocarbons from methane to solid waxes together with smaller amounts of naphthenes and aromatic hydrocarbons. These oils on distillation leave a residue of solid paraffin wax. (The hydrocarbons from  $C_{18}H_{38}$  to  $C_{35}H_{72}$  are semi-solid, called waxes).

(ii) **Asphaltic-base type crude oil.** They contain mainly cycloparaffins (or naphthenic hydrocarbons) with smaller amounts of paraffins and aromatic hydrocarbons. These oils on distillation leave behind asphalt or bitumen.

(iii) **Mixed-base type crude oil.** They contain both paraffinic and asphaltic hydrocarbons and are, generally, rich in semi-solid waxes.

#### 14.4 Refining of Crude Oil

The crude oil is separated into various fractions (having different boiling ranges) by fractional distillation. These fractions are finally converted into desired specific products by removing objectionable impurities. The process is called "*refining of crude oil*" and the plants set up for this purpose are called *oil refineries*.

The processes of refining involve the following stages :

(a) **Separation of water (Cottrell's process).** The crude oil is separated from water by allowing the crude to flow between two highly charged electrodes. The colloidal water-droplets coalesce to form large drops, which separate out from the oil.

(b) **Removal of harmful sulphur compounds.** Sulphur compounds are removed by treating the crude oil with copper oxide. Treatment results in the formation of copper sulphide in solid form which can be removed by filtration.

(c) **Fractional distillation.** The crude oil is heated to about  $400^{\circ}\text{C}$  in a pipe still whereby all volatile constituents are evaporated. The hot vapours are then passed through a tall cylindrical tower, known as *fractionating column*, containing a number of horizontal stainless steel trays at short distances. These trays are provided with individual chimneys which are covered with a loose cap. As the vapours go up, fractional condensation takes place at different heights of column. Higher boiling fractions condenses first ; while the lower boiling fractions condenses later as shown in Fig. 16.

- Condensed liquid runs down from tray to tray through overflow pipes.
- Vapour rises from tray to tray by bubbling through the condensed liquid by raising the bell cap.

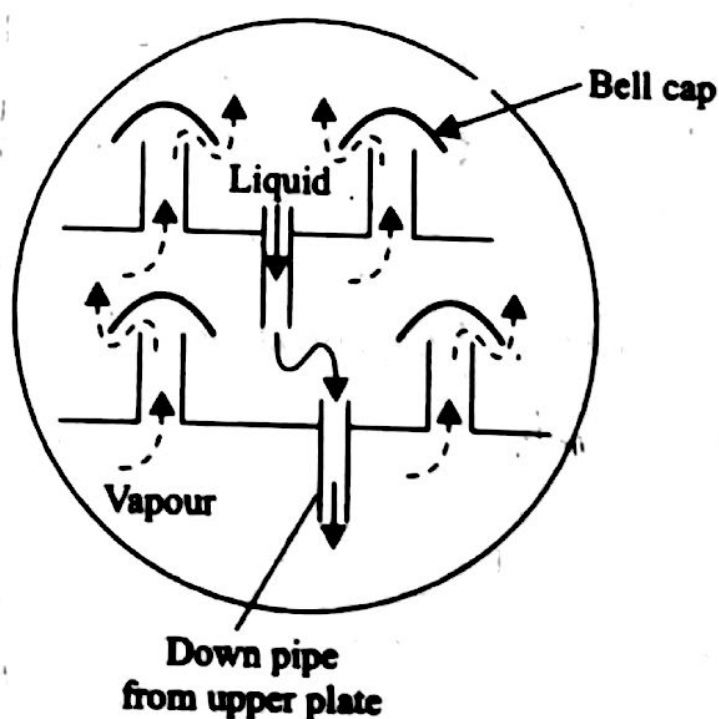


Fig. 16. Fractional distillation of crude petroleum.

Various principal fractionation products are given in Table 8.



Table 8 : Major Fractions Obtained by Distillation of Crude Oil

S.No.	Fraction's Name	Boiling temperature	Approx. composition in terms of hydrocarbon containing C atoms	Applications
1.	Uncondensed gas. (Refinery gas)	<30° C	C <sub>1</sub> to C <sub>4</sub> (such as ethane, propane, isobutane) Lower Hydrocarbons	Used as domestic industrial fuel under the name L.P.G. (liquefied petroleum gas). Used as a solvent.
2.	Petroleum ether.	30° to 70° C	C <sub>5</sub> - C <sub>7</sub>	
3.	Gasoline or petrol or motor spirit.	40 to 120° C	C <sub>5</sub> - C <sub>9</sub> (calorific value = 11,250) kcal/kg	Used as fuel for IC engines, solvent and in dry cleaning.
4.	Naphtha or solvent spirit.	120 to 180° C	C <sub>9</sub> - C <sub>10</sub>	As solvent for paints and varnishes and in dry cleaning.
5.	Kerosene oil.	180 to 250° C	C <sub>10</sub> - C <sub>16</sub> (calorific value = 11,000 kcal/kg)	As an illuminant jet engine fuel and for preparing laboratory gas.
6.	Diesel oil or fuel oil or gas oil.	250 to 320° C	C <sub>10</sub> - C <sub>18</sub> (calorific value = 11,000 kcal/kg)	used as diesel engine fuel.
7.	Heavy oil.	320 to 400° C	C <sub>17</sub> - C <sub>30</sub>	For getting gasoline by cracking.
	This on re-fractionation gives :			
(i)	Lubricating oil.			As lubricants
(ii)	Petroleum jelly. (Vaseline)			In cosmetics and medicines.
(iii)	Grase.			As lubricant.
(iv)	Paraffin wax.			In candles, boot polishes, wax paper, tarapaulin cloth, etc.
8.	Residue may be either :	> 400° C	C <sub>30</sub> and above	used for Water-proofing of roofs and road making.
(i)	Asphalt.			
(ii)	or Petroleum coke.			As a fuel and in moulding arc light rods.

### 14.5 Top-flashing

This is another type of fractionation in which the crude oil is heated in a pipe still and the vapours are passed through different fractionating columns one by one, each of which is maintained at different specific temperatures to collect particular fractions.

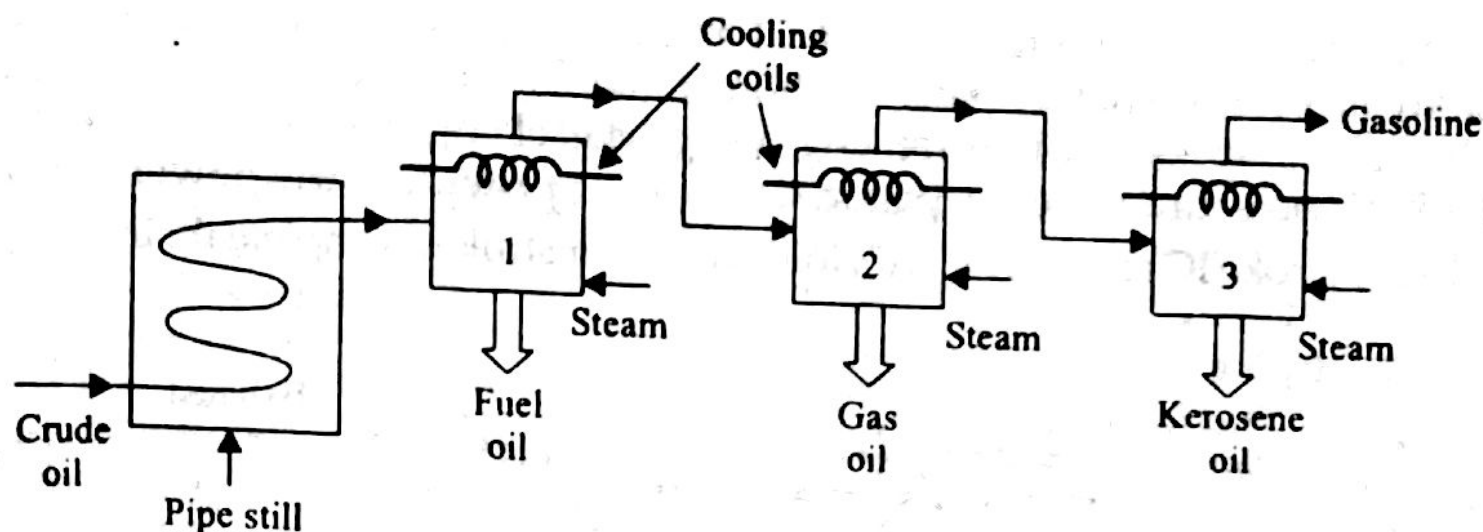


Fig. 17. Top-flasher

The vapours when passed in the first fractionating column (1), condense only fuel oil fraction. The remaining vapours are now passed to the second column (2) which is maintained at such temperature that only gas oil fraction condenses and so on, steam is injected at the bottom of each fractionating column for its partial pressure effect. Finally, vapours of gasoline pass out from the top.

Although top-fresher requires more pumps, cooling coils and instruments but the composition of the products can be better controlled in the more expensive top-flashing process.

#### 14.6 A brief description of three most important liquid fuels viz. gasoline, kerosene and diesel oil is given below :

(a) **Gasoline or petrol fraction.** It is a mixture of hydrocarbons from pentane to octane. This fraction is obtained between 40 to 120 °C. This fraction is highly volatile and inflammable and used as fuel for internal combustion (IC) engines. Its calorific value is about 11,250 cal/gm.

(b) **Diesel oil.** It is a mixture of higher hydrocarbons ( $C_{15}$  to  $C_{18}$ ). This fraction is obtained between 250 to 320° C. It is used as a fuel for diesel engine and its calorific value is about 11,000 cal/gm.

(c) **Kerosene oil.** It is a mixture of hydrocarbons ( $C_{10}$  to  $C_{16}$ ). It does not vaporise easily. It is used as domestic fuel in stoves, as jet engine fuel and for making oil gas. Its calorific value is about 11,100 cal/gm.

Table 9 : Comparison of Gasoline Fuel with Diesel Fuel

S.No.	Characteristics	Gasoline Fuel	Diesel Fuel
1.	Cost	Costly	Cheap
2.	Consumption per unit of power produced	More	Less
3.	Thermal efficiency	Low	High (about 30 – 35%)
4.	Nature of exhaust gases	Polluting and formed in higher amounts.	Polluting and formed in lesser amounts.
5.	Combustion process	Requires simple internal combustion engine since compressed air is not needed for combustion of gasoline.	Requires compressed air and complex, more expensive fuel injection device.

## 15 FUELS FOR INTERNAL COMBUSTION (IC) ENGINES

In an IC engine, a mixture of fuel and air is ignited in a cylinder, either by means of an electric spark (spark-ignition engine e.g. petrol engine) or by compressing the air (compression-ignition engine e.g., diesel engine) and the gases evolved under high pressure force the piston down, thus providing the power stroke.

In a 4-stroke IC engine (Fig. 18), following four strokes complete their working cycle:

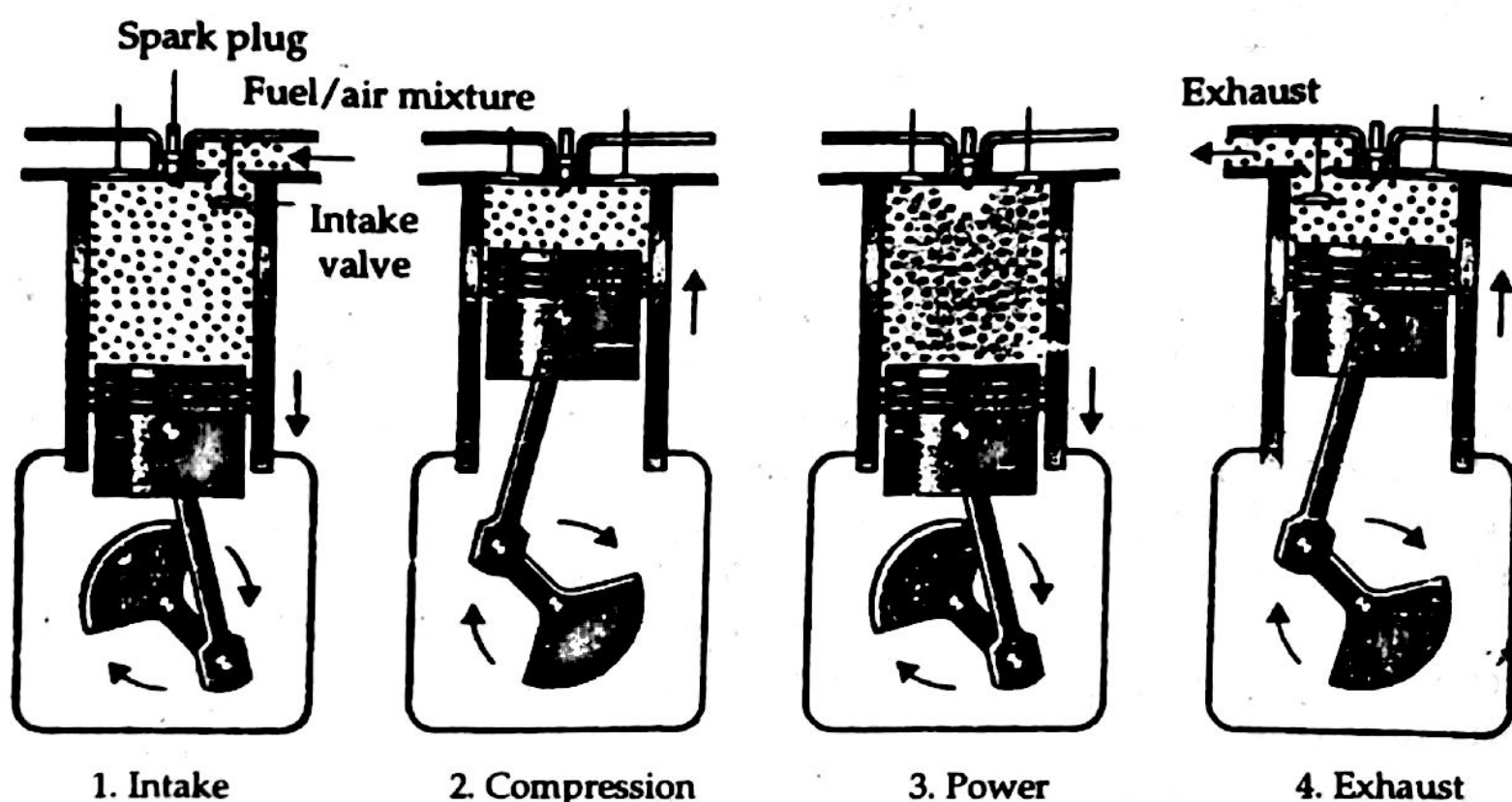


Fig. 18. The operation of a four-stroke engine can be divided into four cycles : intake, compression, power, and exhaust stages.

**1. Intake stroke.** A mixture of fuel vapour and air is drawn into the cylinder during the suction stroke of the cycle.

**Note.** Gasoline in petrol is a liquid at ordinary temperatures but evaporates readily (boiling point range  $30^{\circ} - 200^{\circ}\text{C}$ ) in air to form an easily inflammable mixture.

**2. Compression Stroke.** The piston compresses the mixture in the compression part of the cycle.

**3. Power Stroke.** Spark ignites compressed air-gasoline mixture in the immediate vicinity of the spark plug. The hot gaseous products of combustion expand and a flame front travels at regular and orderly rate through the remainder of the fuel mixture. The hot products of combustion increases the pressure and pushes the piston out, providing an output of power.

**4. Exhaust Stroke.** In the last part (Exhaust stroke) of the cycle the piston ascends and expels the exhaust gases from the cylinder.

A second cycle starts again with the piston descending down.

For optimum efficiency, the following points are worth consideration :

The fuel must completely evaporate in the carburetter and if it does not, there is incomplete combustion and this leads to 'starting-trouble', experienced especially during winter. In summer, the engine will be hot and even if some oil-drops instead of vapour are drawn into the cylinder, they are instantaneously vaporized and starting is easy. However, if the fuel evaporates before setting into the carburetter, the vapour lock formed in the fuel supply line stops the engine. The vapour pressure should not exceed  $0.63 \text{ kg/cm}^2$  (about 9 psi) for gasolines used in summer and  $0.77 \text{ kg/cm}^2$  (about 11 psi) for those in winter months.



Aviation gasoline should not have vapour pressure exceeding  $0.49 \text{ kg/cm}^2$  (about 7 psi).

Another problem arising out of any less volatile, unburnt fuel remaining in the cylinder is the dilution of lubricating oil. This promotes friction and wear.

A brief comparison of Petrol and Diesel engines is given in Table 10.

**Table 10 : Comparison of Petrol and Diesel Engines**

S.No.	Description	Petrol Engine	Diesel Engine
(i)	Fuel	(Petrol + air) mixture	(Diesel + air) mixture
(ii)	Ignition	By spark plug	By compression of air
(iii)	Cause of knocking	Pre-ignition	Delayed-ignition
(iv)	Knocking characteristics expressed in	Octane rating	Cetane rating
(v)	Examples of additives to reduce knocking	TEL, Diethyl telluride	Alkyl nitrites

## 16 KNOCKING

### Terminology :

(a) **Ignition temperature.** It is the minimum temperature at which the combustion is self-supporting. This is also referred to as *spontaneous ignition temperature (SIT)*.

(b) **Compression ratio.** The power output and efficiency of an IC engine depends on a factor called *compression ratio (CR)*. It is defined as the ratio of gaseous volume ( $V_1$ ) in the cylinder at the end of the suction-stroke to the volume ( $V_2$ ) at the end of compression-stroke of the piston,

$$\text{As } V_1 > V_2 \Rightarrow \text{CR} = \frac{V_1}{V_2} > 1.$$

The CR obviously indicates the extent of compression of fuel-air mixture by the piston.

### Knocking and compression ratio

The fuel-air mixture gets heated to a temperature greater than its ignition temperature as a result of compression. This leads to spontaneous combustion even before sparking.

It is also possible that the last portion of the fuel-air mixture undergoes self-ignition after sparking. It is due to the heating and compression of the unburned fuel, by the spreading flame-front sweeping across the cylinder.

The resulting shock wave dissipates its energy by hitting the cylinder walls and the piston. In view of the characteristic rattling sound emitted, this is called *knocking*. The CR at which fuel tends to knock is called *critical compression ratio*.

When the compression ratio exceeds the critical compression ratio limit, the ignition temperature of the fuel gets reduced and the ignition of fuel takes place before the piston head reaches the end of the compression stroke. As a result, combustion of fuel takes place much rapidly. The remaining fuel in the cylinder burns in an explosive manner and disorderly fashion ahead of the flame front and so produces the characteristic rattling sound called "*knocking*".

- When ignition of fuel/air mixture takes place at the right time, the fuel power generated is utilized in driving the internal combustion engines of scooters, cars etc.

- When ignition occurs much earlier, that is before the end of compression stroke, the combustion energy is lost in producing metallic sound, called as knocking.
- **Knocking** is thus a sharp metallic sound similar to rattling of hammer which is produced in the internal combustion engine due to immature ignition of the air/fuel mixture.

*To Summarize :* With increase in CR, efficiency of IC engine also increases but after critical CR, tendency to knock also increases.

*Consequences of knocking :*

- Decreased power output,
- Mechanical damage by over heating of the cylinder parts.

*Probable Mechanism of chemical reactions that lead to knocking*

Free radical chain reaction leading to Cracking and Oxidation of the hydrocarbons is probably the mechanism of chemical reactions that lead to knocking.

*Factors on which knocking depends :*

- Engine design
- Running conditions and
- Chemical structure of the fuel hydrocarbons.* For instance :
  - knocking tendency decreases in the order —

$n$ -alkanes > mono-substituted alkanes > cyclo alkanes > alkenes > poly substituted alkenes > aromatics.

And for straight chain hydrocarbons, the tendency to knock increases with molecular weight and boiling point, e.g.,  $n$ -hexane >  $n$ -pentane >  $n$ -butane.

Aromatic hydrocarbons have higher antiknocking properties than paraffins and olefins.

## 17 OCTANE NUMBER

The resistance offered by gasoline to knocking cannot be defined in absolute terms. It is generally expressed on an arbitrary scale, known as **Octane rating** (proposed by Graham Edgar in 1926).

Fuel	Octane number	Characteristics
$n$ -heptane	0	Knocks severely
Isooctane	100	High resistance to knocking

The % of isooctane in the  $n$ -heptane — isooctane blend which has the same knocking characteristics as the gasoline sample, under the same set of conditions is known as *octane number*.

### 17.1 Influence of structure of the fuel on the octane rating :

- As straight chain (or normal) hydrocarbons knock severely in petrol engines so they have lowest octane numbers.
- As the knocking tendency of  $n$ -alkanes increases with the increase in the length of carbon chain so anti-knocking properties (and thus octane numbers) also decrease with increase in the length of the carbon chain.

For example :

<i>n</i> -paraffin	Octane number
Methane	122
Ethane	101
Propane	96
<i>n</i> -butane	89
<i>n</i> -pentane	60
<i>n</i> -hexane	29
<i>n</i> -heptane	0
<i>n</i> -nonane	- 45

- (iii) Branched chain paraffins have lower tendency to knock so they have higher anti-knock properties (and thus octane numbers) in comparison to normal chain paraffins.

Furthermore, resistance to knock increases with the number of branches and their position.

For example :

Hydrocarbon	<i>n</i> -heptane	2-methyl hexane	2, 2-dimethyl pentane
Octane number	0	55	80

Recently, the hydrocarbon 2, 2, 3 - trimethylpentane called **triptane** has been assigned an octane number, 125.

- (iv) Knocking tendency decreases with the increase in the number of carbon-carbon double bonds in the hydrocarbon fuel.

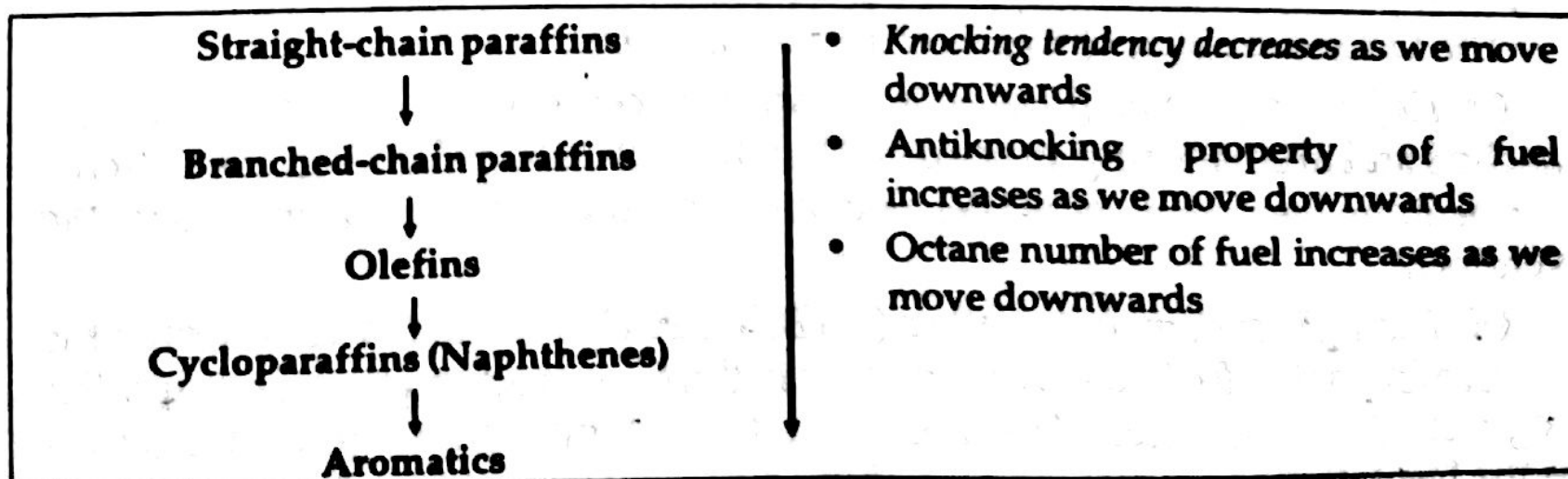
Thus, olefins have higher anti-knock properties (and thus octane number) than the paraffins of same carbon-chain length.

Furthermore, the anti-knocking tendency (and thus octane number) increases as the position of the double bond approaches the centre of chain.

- (v) The knocking tendency decreases with increase in the compactness of the molecules. As a result, octane number of cyclo-paraffins (Naphthenes) are higher than *n*-alkanes, branched-alkanes and alkenes.
- (vi) Aromatic hydrocarbons such as benzene and toluene have less knocking tendency than naphthenes so their octane numbers are highest.

Fuel	<i>n</i> -hexane	Cyclohexane	Benzene
Octane number	26	77	100 +

To sum up





(vii) In cracked and reformed gasoline, it is the presence of olefins, iso-paraffins and aromatic hydrocarbons that increase its anti-knocking properties and thus the octane number.

Note. Gasoline used in automobiles should have an octane number 80 or higher, while gasoline used in aeroplanes has an octane numbers 100 or even higher.

Engine	rpm	Fuel	Cetane number	Application
Low speed diesel engine	150 – 500	Low speed diesel fuel	$\geq 25$	Ships
Medium speed diesel engine	500 – 1500	Medium speed diesel fuel	$\geq 35$	Tractors or locomotives
High speed diesel engine	1500 – 2000	High speed diesel fuel	$\geq 45$	Trucks and buses

**Additives for improving antiknock properties.** Tetra ethyl lead (TEL) and diethyl telluride ( $(C_2H_5)_2Te$ ) are the most commonly used additives.

TEL gives rise to Pb and PbO during combustion. These particles act as free-radical chain inhibitors as they arrest the propagation of the explosive chain reactions responsible for knocking

Efficiency of TEL decreases in presence of sulphur hence Desulphurized Gasoline is preferred.

Pb and PbO<sub>2</sub> decrease engine life hence they must be removed along with exhaust gases by adding ethylene dibromide.

$(Pb, PbO_2 + C_2H_4Br_2 \longrightarrow PbBr_2)$ . Because PbBr<sub>2</sub> formed is volatile it escapes into atmosphere. But pollution problem still exists.

Another cause of pollution is incomplete combustion leading to the formation of CO, NO, NO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub> etc. Hence catalytic convertors based on Pt are employed which will catalyze combustion reaction to completion.

e.g.,  $CO \longrightarrow CO_2$

But Pt is poisoned by Pb, so Unleaded Petrol should be used.

Benzene is added for decreasing knocking. Since benzene is carcinogenic, very low concentration of benzene should be used.

## 18 UNLEADED PETROL

The petrol whose octane number is increased without the addition of lead compounds is referred to as unleaded petrol.

The Octane number of a fuel can be increased by :

(i) **Reforming.** This process increases the contents of molecules having branched and aromatic ring structures. Thus, by molecular reforming, the contents of isopentane, isooctane, ethyl benzene and isopropyl benzene increases in the given fuel.

(ii) **Methyl tertiary butyl ether (MTBE)**, can also be added to improve the octane rating of the fuel. MTBE has oxygen in the form of ether group and supplies oxygen for the combustion of the petrol in internal combustion engine thus reducing the formation of peroxy compounds.

*Advantages of using unleaded petrol :*

Because of the absence of lead

- (i) unleaded petrol is free from lead-pollution.
- (ii) it allows the use of a catalytic converter to be attached to the exhaust in the automobiles.

**Note :** Catalytic converter contains a rhodium catalyst which converts toxic gases like CO, NO etc. into harmless gases like CO<sub>2</sub>, N<sub>2</sub> etc. It also oxidises unburnt hydrocarbons into CO<sub>2</sub> and H<sub>2</sub>O. Lead poisons the Rh catalyst by destroying the active sites.

## 19 DIESEL (OR COMPRESSION IGNITION) ENGINE AND CETANE NUMBER

In the diesel engine, air is first drawn into the cylinder and compressed to a pressure of about 500 psi ( $3.52 \times 10^5$  kg/m<sup>2</sup>). This compression is accompanied by a rise in temperature to about 500 °C.

Towards the end of the compression stroke, diesel is injected in the form of finely-divided spray into air in the cylinder heated to about 500 °C by compression.

The oil absorbs the heat from the air and it ignites spontaneously as it attains ignition temperature. This raises the temperature and pressure. The piston is pushed by expanding gases in the power stroke.

The combustion of fuel in a diesel engine is not instantaneous, the interval between the start of fuel injection and its ignition is called 'the *ignition delay*'.

Ignition delay is *due to* the time taken for the vaporization of the individual droplets and raising of the vapour to its ignition temperature.

It depends on the (a) Engine design ; (b) Efficiency of mixing of the spray and air ; (c) The injector design and (d) Mostly on the chemical nature of the fuel.

e.g., ignition delay is shorter for paraffinic fuel, than for olefinic, naphthalenic and aromatic fuels.

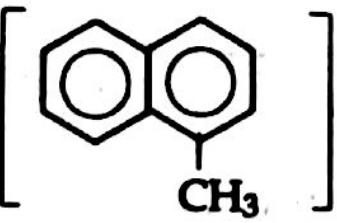
If the ignition delay is long, it will lead to fuel accumulation in the engine even before the ignition. When ignited, an explosion results as the combined effect of increased temperature and pressure. This is responsible for *diesel knock*.

The diesel fuel should have a spontaneous ignition temperature less than the temperature produced by compression.

As the temperature to which air can be heated by compression is limited by various constraints, it is desirable to have fuels with short ignition delay but the ignition delay must be long enough for the compression stroke to be completed.

In order to grade the diesel fuels, cetane rating is employed.

**Cetane number.** It is a measure of the ease with which a fuel will ignite under compression.

Diesel fuel	Cetane no.	Remarks
Cetane C <sub>16</sub> H <sub>34</sub> [or CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CH <sub>3</sub> , <i>n</i> -hexadecane]	100	Very short ignition delay
$\alpha$ -methyl naphthalene 	0	Longer ignition delay

Cetane no. of fuel primarily depends on the nature and composition of its hydrocarbons.



For instance, consider the following series :

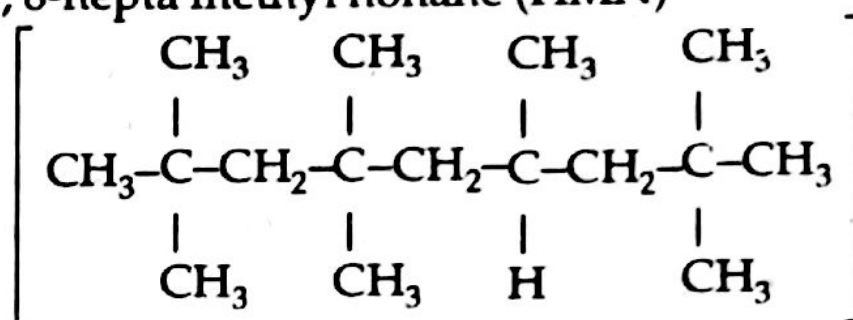
*n*-alkanes > naphthenes (i.e., cycloalkanes) > alkenes > branched alkanes > aromatics

- ignition delay increases from left to right
- ignition quality increases from right to left
- cetane no. increases from right to left.

As, straight chain alkanes like *n*-cetane have low ignition delay (high ignition quality) and ignite readily on compression, while aromatics do not ignite readily on compression, we can say that high cetane-no. fuels eliminate diesel knock.

The cetane no. of diesel fuel may be raised by the addition of pre-ignition dopes such as alkyl nitrites such as ethyl nitrite, amyl nitrite etc.

2, 2, 4, 4, 6, 8, 8-hepta methyl nonane (HMN)



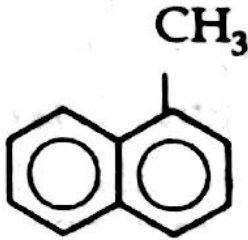
with a cetane rating of 15 is now considered as the low quality diesel in view of its easy availability and purity.

On the revised scale (HMN reference) the cetane number (CN) represents the % cetane in the blend with HMN plus  $\frac{15}{100}$  of the % HMN.

Thus, a blend of 50% cetane and 50% HMN has a cetane rating of

$$50 + \frac{15}{100} \times 50 = 57.5.$$

The differences between the Octane number and Cetane number are summarized below :

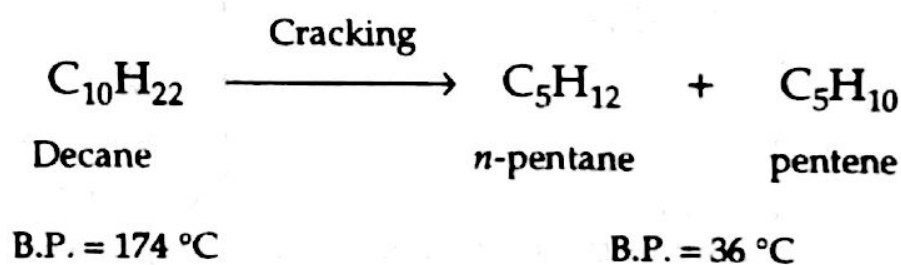
S.No.	Octane No.	Cetane No.
1.	<p>It is the % of <i>iso</i>-octane in a mixture of <i>isooctane</i> (2, 2, 4-trimethyl pentane) and <i>n</i>-heptane, which matches the fuel under test in knocking characteristics. e.g., an 60-octane fuel is one which has the same combustion characteristics as a 60 : 40 mixture of <i>iso</i> octane and <i>n</i>-heptane.</p> <p style="text-align: center;"><math>\text{CH}_3 - (\text{CH}_2)_5 - \text{CH}_3</math>; <i>n</i>-Heptane Knocks very-badly (Octane no. = 0)</p> <p style="text-align: center;"> <math>\begin{array}{cc} \text{CH}_3 &amp; \text{CH}_3 \\   &amp;   \\ \text{CH}_3 - \text{C} - \text{CH}_2 - &amp; \text{C} - \text{CH}_3 \\   &amp;   \\ \text{CH}_3 &amp; \text{H} \end{array}</math> </p> <p style="text-align: center;"><b>Isooctane 2,2,4-Trimethyl Pentane</b> Gives very little knocking (Octane no. = 100)</p>	<p>It is the % of hexadecane in a mixture of hexadecane and 1-methyl naphthalene which have the same ignition characteristics as the diesel fuel in question.</p> <p style="text-align: center;">  </p> <p style="text-align: center;"><b>1-methyl naphthalene</b> (Cetane no. = 0)</p> <p style="text-align: center;"><math>\text{CH}_3 - (\text{CH}_2)_{14} - \text{CH}_3</math> <b><i>n</i>-Hexadecane</b> (Cetane no. = 100)</p>



S.No.	Octane No.	Cetane No.
2.	It is used for finding suitability of gasoline or any other internal combustion engine fuel.	It is used for finding suitability of a diesel fuel.
3.	The Octane number of I.C. fuels can be raised by the addition of tetraethyl lead $(C_2H_5)_4 Pb$ or TEL and Diethyl telluride $(C_2H_5)_2 Te$ .	The cetane number of diesel fuel can be raised by the addition of small quantity of certain 'Pre-ignition dopes' like ethyl nitrite, isoamyl nitrite, acetone peroxide etc.
4.	Hydrocarbons which are poor diesel fuels are quite good gasoline fuels.	Ignition quality order among hydrocarbon constituent of a diesel fuel is as follows : $n$ -alkanes > naphthalenes > alkenes > branched alkanes > aromatics. Thus, hydrocarbons which are poor gasoline fuels are quite good diesel fuels.
5.	Straight chain hydrocarbon molecules are worst fuels. As they have low-Octane numbers.	Straight chain hydrocarbon molecules are best, as they have high cetane numbers.

## 20 CRACKING

Cracking is defined as the decomposition of high molecular weight hydrocarbons of high boiling points into simpler, lower molecular weight hydrocarbons of low boiling points.

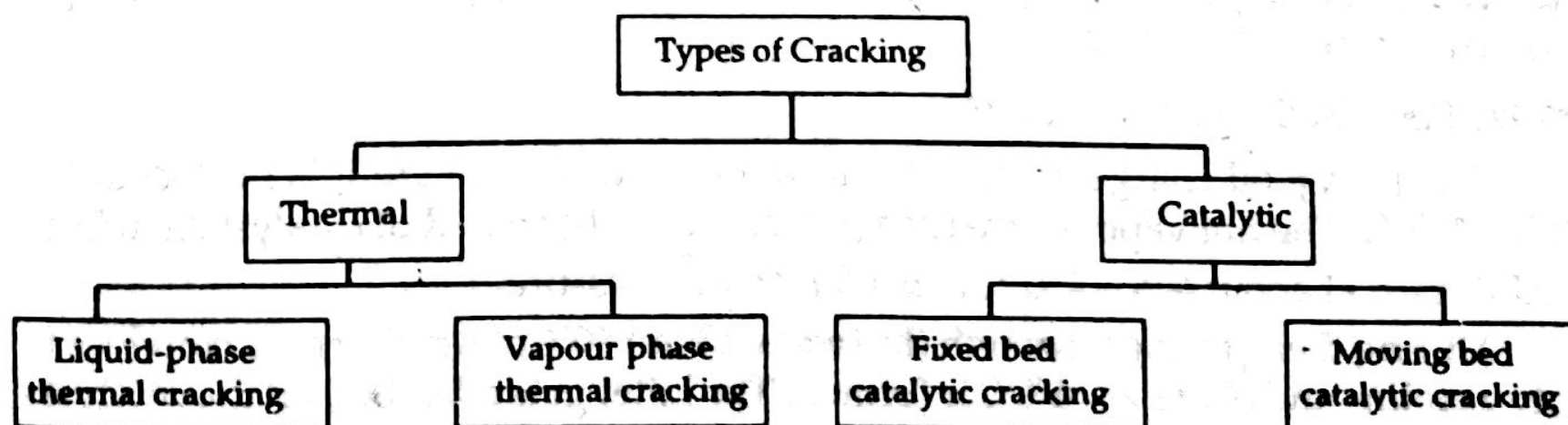


**Importance.** Of all the fractions obtained by fractionation of petroleum, gasoline has the highest demand as a motor fuel, but the yield of this fraction is only 20% of the crude.

Also the quality of so-called 'straight-run' gasoline is not so good.

Hence, it is used only after suitable blending. Moreover, there is a surplus of heavier petroleum fractions. To overcome these difficulties, the middle and heavy fractions are cracked to get more valuable low boiling fractions.

For instance, the petrol made by cracking has far better characteristics (as far as the IC engine is concerned) than 'straight-run' petrol.



### 20.1 Thermal Cracking

When the heavy oils are subjected to high temperature and pressure in the absence of catalyst, it is called thermal cracking. In a thermal cracking process, the heavy oil residue (from primary distillation of crude oil)

- (a) is heated to a temperature greater than its boiling point to promote rupture of the carbon-carbon bonds and
- (b) subjected to high pressures to prevent the vaporization of the cracked residues.

In thermal cracking the bigger hydrocarbon molecules break down to give smaller molecules of the paraffin, olefins plus some hydrogen. It is of two types viz. liquid and vapour phase thermal cracking. The operating conditions depend on the desired product. Low pressures and high temperature (that is conditions for vapour phase thermal cracking) tend to produce more low-molecular weight and volatile hydrocarbons than those produced under high pressure and low temperature conditions (that is under liquid phase thermal cracking).

A comparative account of these two is given in Table 11.

Table 11. Comparison of Liquid and Vapour phase Thermal Cracking

Characteristic	Liquid-phase-Thermal Cracking	Vapour Phase-Thermal Cracking
Cracking temperature	475 – 530 °C	600 – 650 °C
Pressure	100 kg/cm <sup>2</sup>	10 – 20 kg/cm <sup>2</sup>
Yield of Petrol	50 – 60%	—
Octane rating of Petrol	65 – 70	(> 70) ∴ Better antiknock characteristics
Criteria	None Any heavy oil can be used	Oil should be readily vaporized.
Time required for cracking	More	Less

### 20.2 Catalytic Cracking

The quality and quantity of gasoline produced by cracking can be greatly improved by using a suitable catalyst-like *aluminium silicate*,  $Al_2(SiO_3)_3$  or Synthetic, hydrated alumino-silicates ( $Al_2O_3 = 12.5\%$  and  $SiO_2 = 87.5\%$ ) or acid-activated natural silicates like montmorillonites or molecular sieves. Catalytic cracking requires much lower temperatures and pressures compared to thermal cracking. There are two types of catalytic cracking, viz. Fixed bed and moving bed catalytic cracking. These are discussed below :

#### 20.2A Fixed-bed Catalytic Cracking

The heavy oil charge is passed through a preheater where it is heated upto 425 – 450°C. The hot vapours are then passed over a fixed bed of catalyst chamber maintained at about 425 – 450°C and 1.5 kg/cm<sup>2</sup> pressure.

During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% C is formed. The latter gets adsorbed on the catalyst

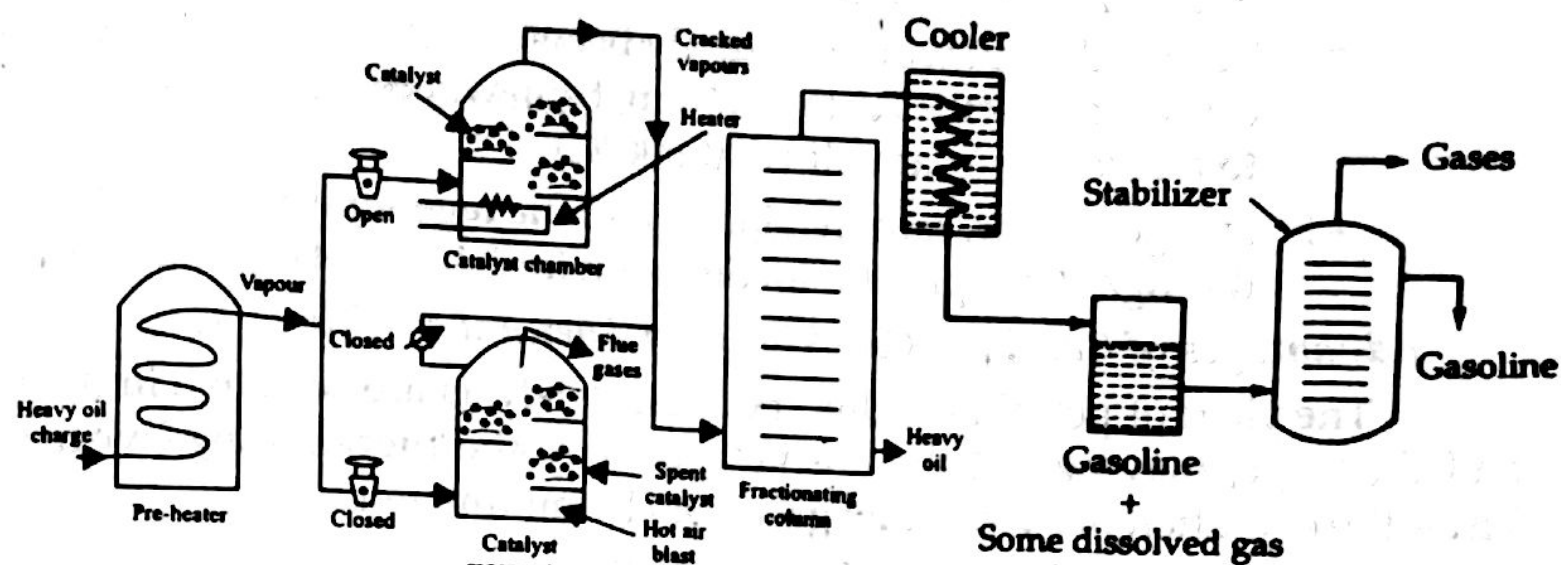


Fig. 19. Fixed bed catalytic cracking process.

bed. The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activation interval, the vapours are diverted through another catalyst chamber.

### 20.2B Moving-bed Catalytic Cracking

In moving bed catalytic cracking, the feed oil is first passed through a pre-heater. The pre-heated oil vapours alongwith very finely powdered catalyst are then passed in a reactor which is maintained at a temperature of  $500^{\circ}\text{C}$  for catalytic cracking. The cracked oil vapours are then passed to the fractionating column where heavy oil is separated. The vapours are then passed through the cooler where gasoline condenses along with some gases. This is then sent to a stabiliser where the dissolved gases are removed and pure gasoline is recovered. The main components along with their functions are discussed with the help of Fig. 20 below :

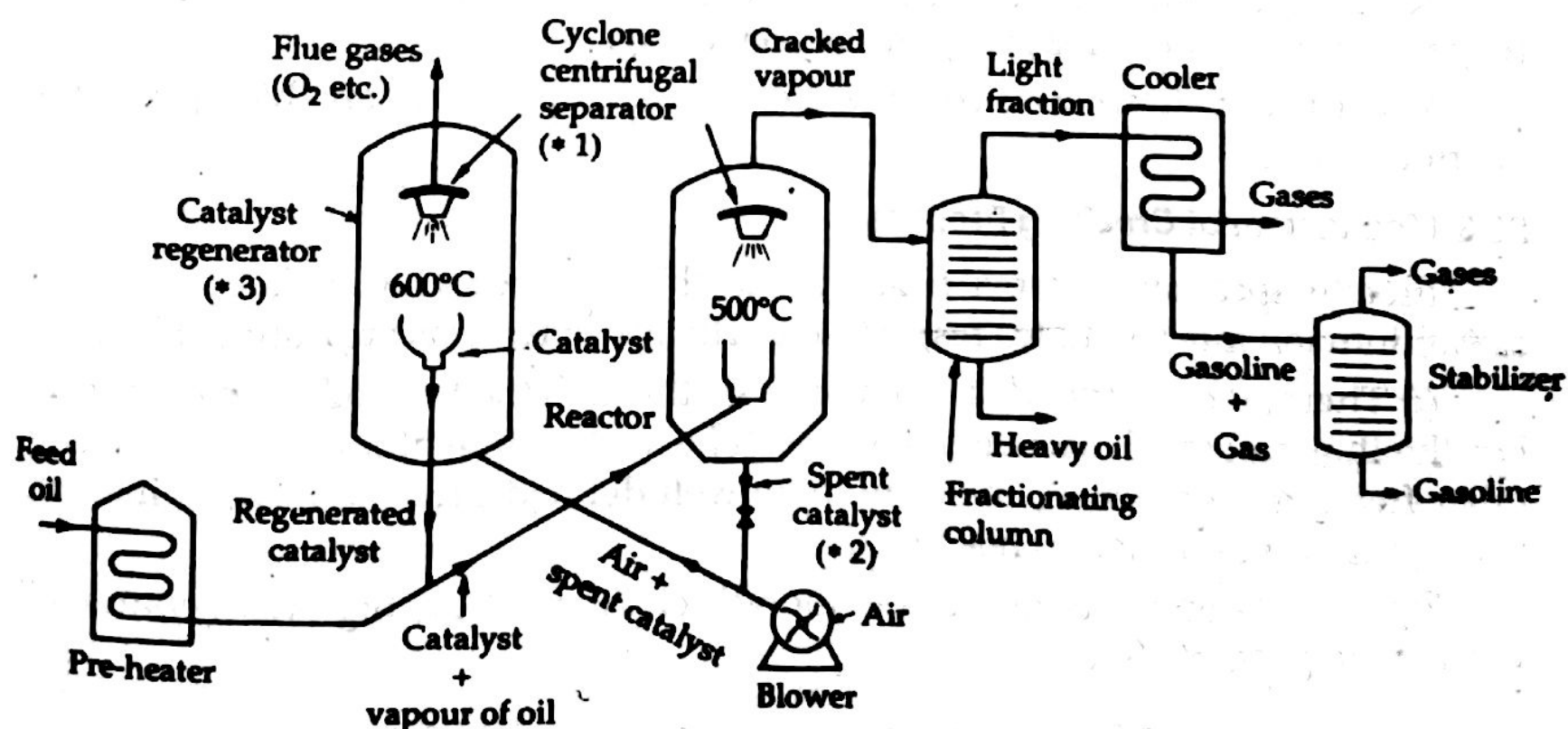


Fig. 20. Moving bed catalytic cracking.



- \* 1 Cyclone allows only the cracked oil vapours to pass on to the 'fractionating column', but retains all the catalyst powder in the reactor itself.
- \* 2 The catalyst powder gradually becomes heavier, due to coating with carbon, and settles to the bottom, from where it is forced by an air blast to regenerator (maintained at 600°C).
- \* 3 In regenerator, carbon is burnt and the regenerated catalyst then flows through stand-pipe for mixing with fresh batch of incoming cracking oil.

**Advantages of Catalytic Cracking over Thermal cracking :**

1. The yield of petrol is higher, because catalysts are selective in their action and therefore, they permit the cracking of only the high-boiling hydrocarbons. Thus, the evolution of by-product gases can be minimized.

**2. The quality of petrol produced is better**

- (i) The product of cracking contains a higher amount of aromatics and hence, it possess better anti-knock characteristic.
- (ii) Isomerization to branched-chain compounds (iso-paraffins) occur, thereby better petrol is produced.
- (iii) The product contains a lesser amount of undesirable sulphur, because a major portion of it escapes as H<sub>2</sub>S gas, during cracking.
- (iv) Decomposition of aromatic removes only the side chains, but no ring itself is broken.

**Note :** Tendency of fuel-constituents to knock : straight chain paraffins > branched-chains paraffins > olefins > naphthalenes > aromatics.

3. No external fuel is necessary for cracking. The heat required for cracking is derived from the coal, embedded in the catalyst.

4. A much lower pressure (about 1 – 5 kg/cm<sup>2</sup>) is needed in catalytic cracking.

5. The cracking process can be easily controlled, so the desired products can be obtained.

6. The % of gum or gum forming compounds is very low.

**Note :** Unsaturated straight chain hydrocarbons which tend to get oxidised and polymerized thereby causing gum formation on storing.

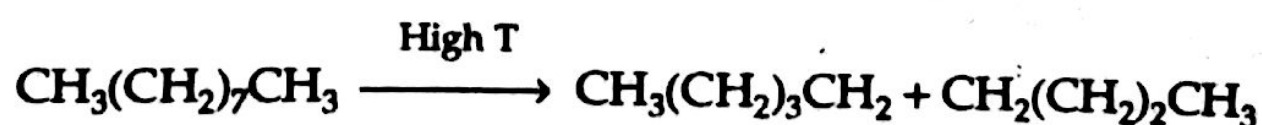
7. The production cost is very low since high temperatures and high pressures are not needed.

### 20.3. Mechanism of Cracking Process

Broadly speaking, Thermal & catalytic cracking processes invoke free radical and carbonium ion intermediates respectively. Their mechanisms are outlined below :

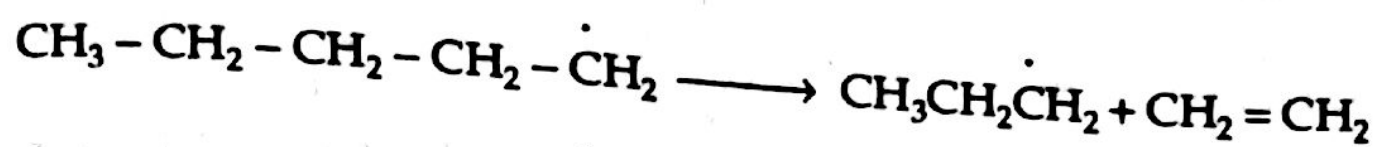
(i) **Thermal cracking.** It is believed to go through the free radical mechanism. For the illustration of mechanism. Let us take an example of *n*-nonane. Like any other free radical reaction, there are three well defined processes, viz., initiation, propagation & termination reactions.

**Initiation :** nonane undergoes homolytic cleavage at the high temperature of cracking to generate free radicals.

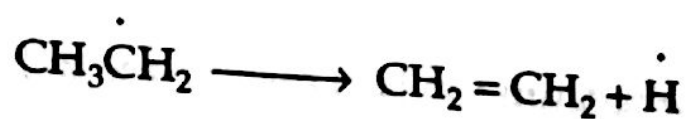


**Propagation :**

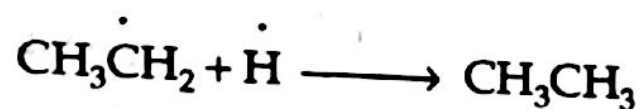
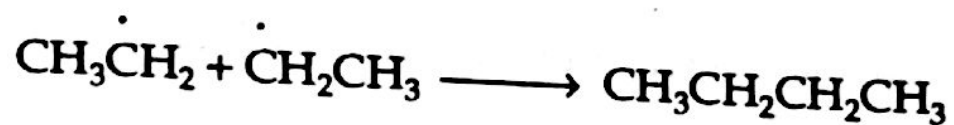
The free radicals formed in the initiation step undergo fission at the  $\beta$ -position to yield a new radical and an olefin. These scission reactions continue until a thermally more stable radical is formed.



The radicals having no C - C bond in the  $\beta$ -position give rise to hydrogen free radical.

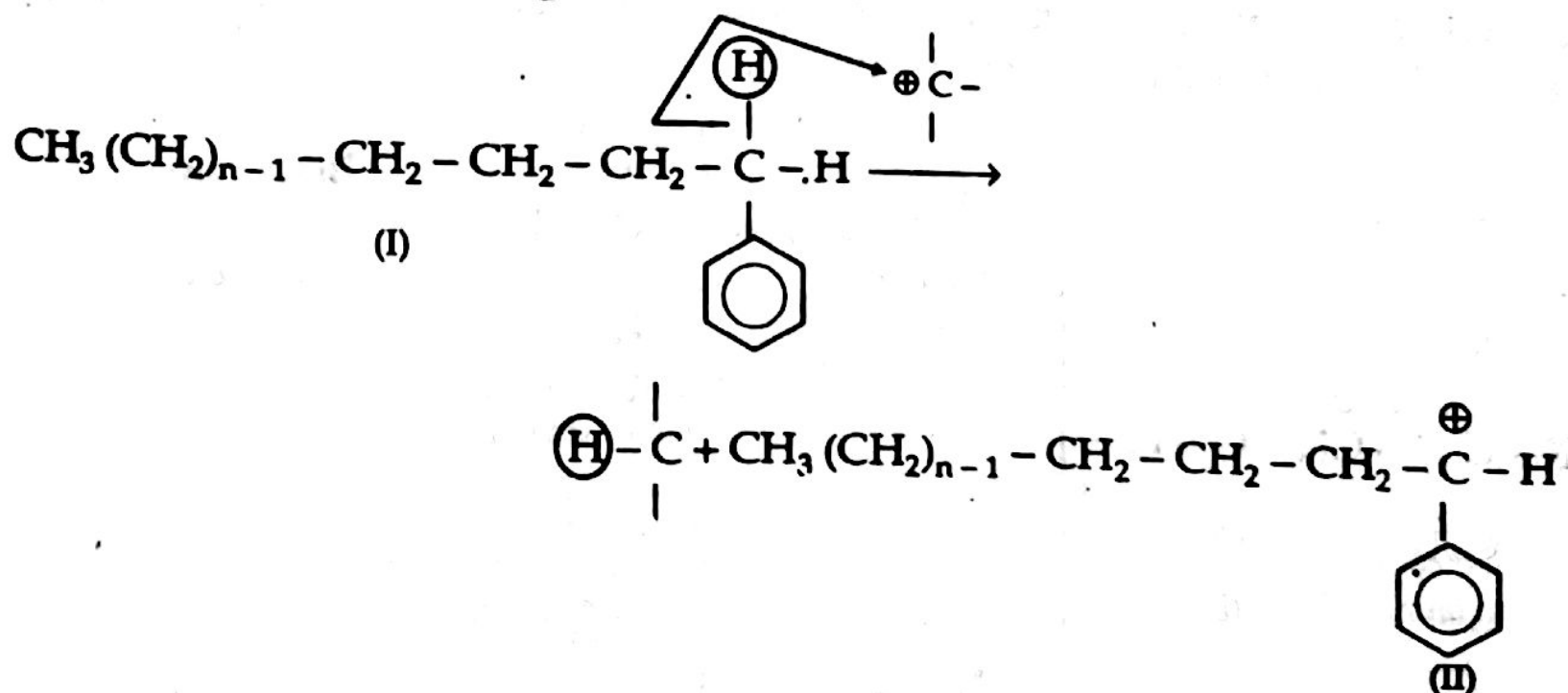
**Termination :**

These cleavage reactions terminate by the coupling of unstable free radical intermediates.



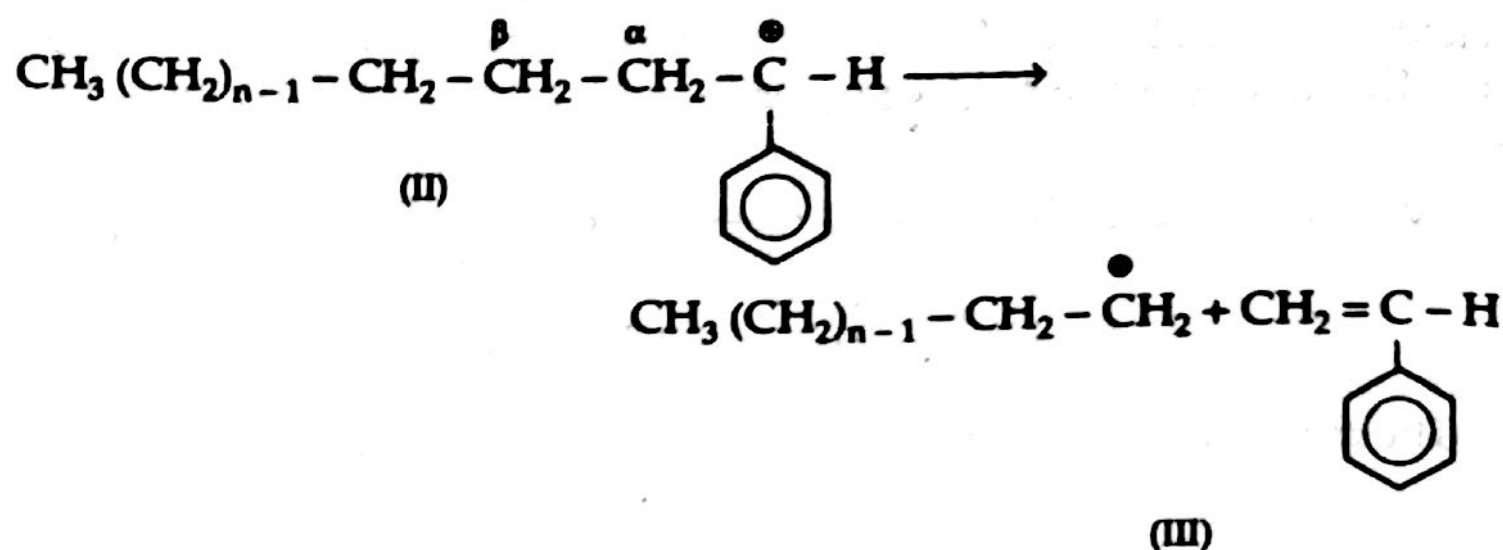
(ii) **Catalytic cracking.** It is believed to involve carbonium-ion intermediates. As the heavy oil is a complex mixture of hydrocarbons so the suggested mechanism is based on investigation on model compounds.

(i) Cracking of aromatic hydrocarbon (I) results in the removal of only the side chains, but no benzene ring itself is broken.

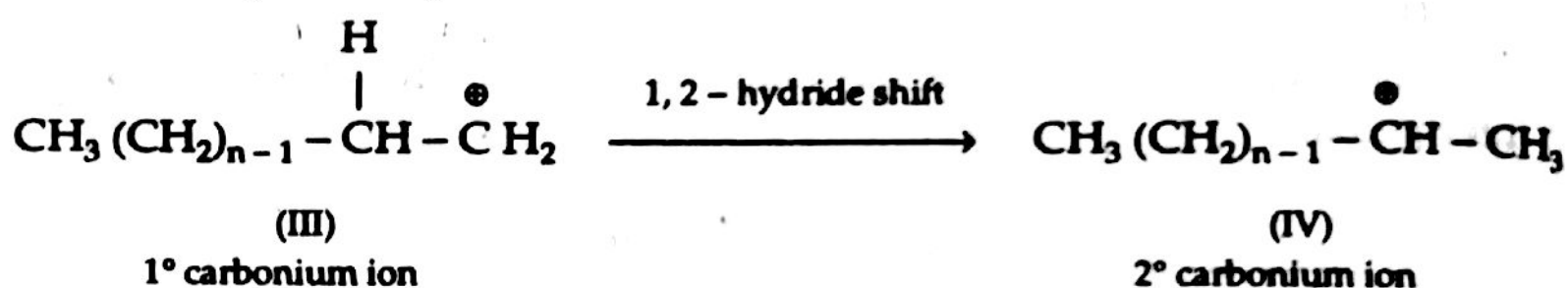


(ii) The carbonium ion (II) undergoes  $\beta$ -cleavage to give an alkene and a smaller carbonium ion.

Cleavage occurs across the C - C bond  $\beta$  to the C atom carrying the positive charge.



(iii) The primary carbonium ion (III) rearranges to the more stable secondary carbonium ion by a 1, 2-hydride shift.

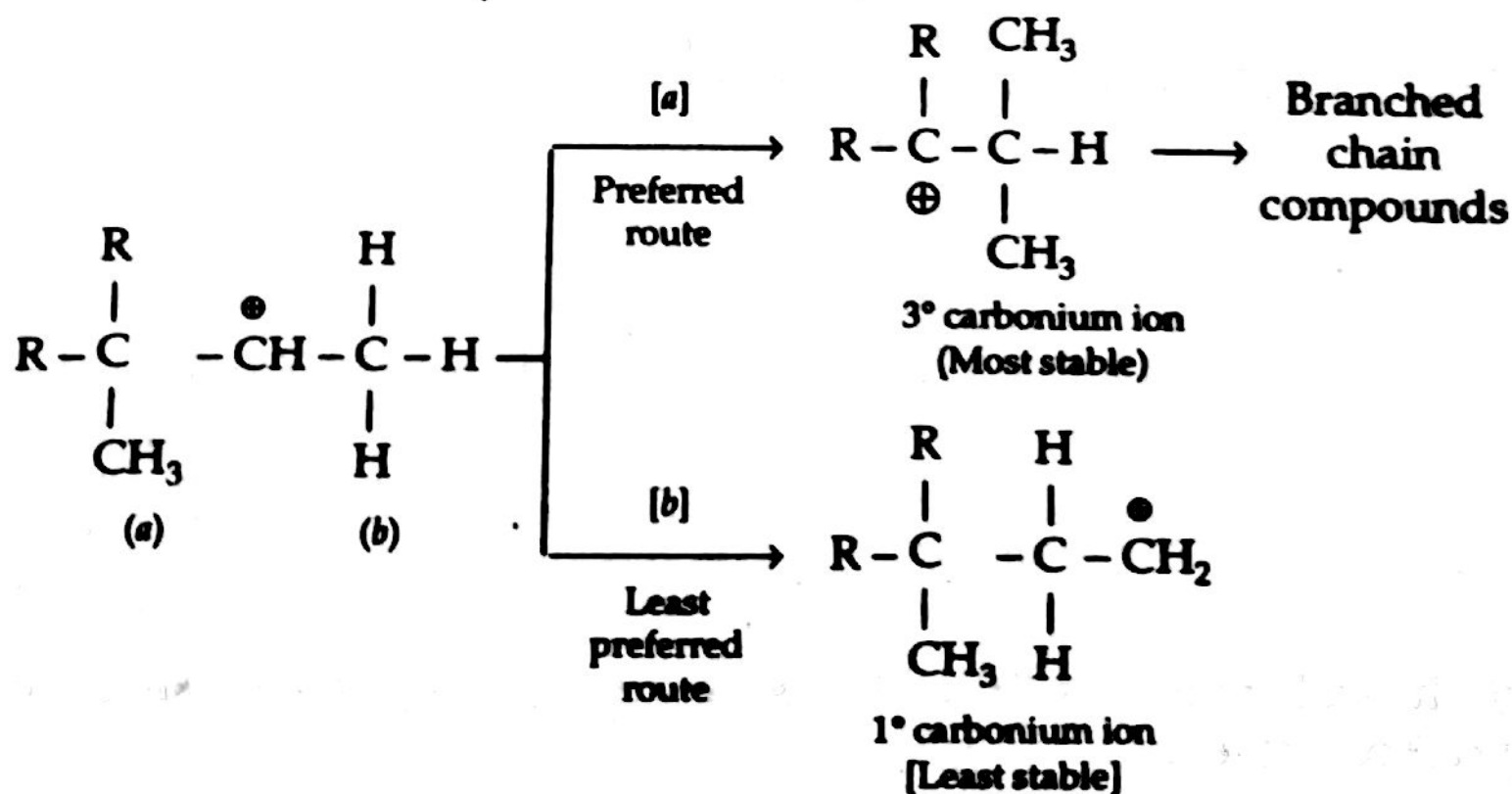


(iv) The smallest alkene which can be formed by  $\beta$ -cleavage of a secondary carbonium ion (IV) is propene.



Subsequently, 1° carbonium ion (V) rearranges to the more stable 2° carbonium ion by 1, 2 - hydride shift.

(v) Whenever a secondary (2°) carbonium ion is formed, it will show tendency to form more stable tertiary (3°) carbonium ion. If 2° carbonium ion has more than four carbon atoms, it will form branched-chain compounds by skeletal rearrangement as it is converted to 3° carbonium ion.

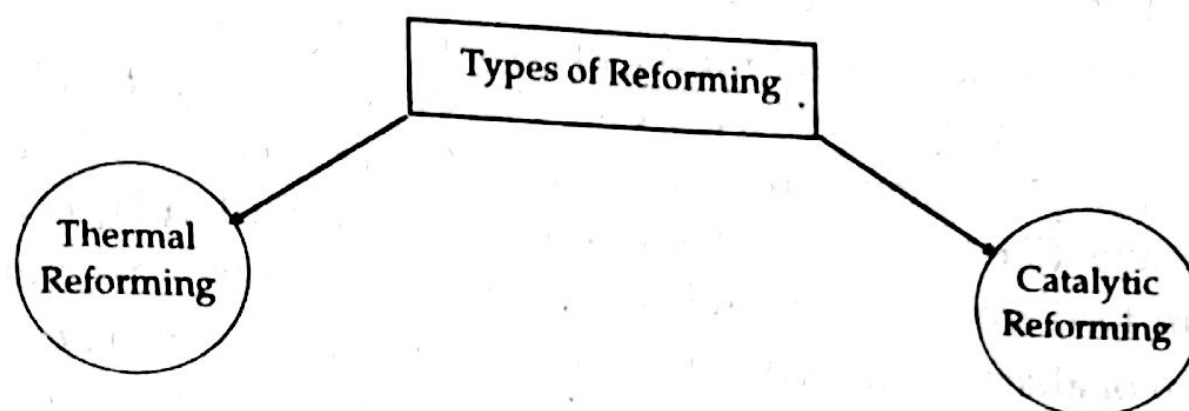




(vi) Aromatic compounds might also form from alkenes and carbonium ion though a sequence of steps involving cyclization, and aromatization.

## 21 REFORMING

The antiknock characteristics of gasoline (prepared by the fractional distillation of crude oil or by cracking) can be improved by 'reforming', which in effect brings about structural modifications in the components of feed-stock either thermally or catalytically.



(i) *Thermal reforming.* It comprises of heating the straight-run gasoline under pressure in the absence of a catalyst. It is carried out in a reactor at  $500 - 600^{\circ}\text{C}$  and a pressure of 85 atmosphere (Fig. 16). The conditions are well controlled to prevent the formation of gas at the expense of gasoline. The product vapours are rapidly cooled (quenched) by a cold-oil spray for controlling the reforming. The reformed products are then fractionated to remove residual gases. During thermal reforming, some cracking also occurs to yield saturated and unsaturated hydrocarbons. Conversion of *n*-alkanes to branched-chain alkanes also takes place during thermal reforming. Other main reactions which take place are : dehydrogenation, cyclization and aromatization.

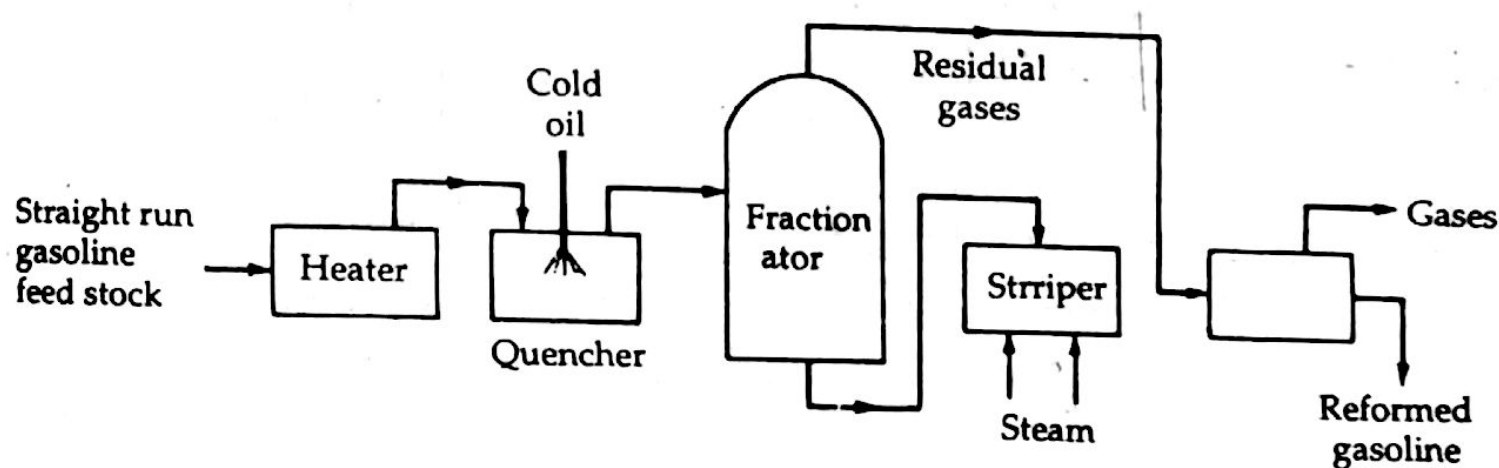


Fig. 21. Thermal reforming of straight run gasoline.

(ii) *Catalytic reforming.* Reforming done in the presence of a catalyst (platinum supported on alumina) is known as catalytic reforming. The quality and quantity of gasoline obtained by catalytic reforming is much better compared to thermal reforming. It is done at  $460 - 530^{\circ}\text{C}$  and 35 – 50 atmospheric pressures by using either a fixed-bed or fluidized bed process. The platinum-catalysed reforming is also known as Platforming.

**Fixed-bed Platforming process.** Flow-diagram of this process is given in Fig. 22. The feed stock is heated and fractionated to remove low-boiling vapours, water and oxygen. This is done to avoid any explosive reaction with hydrogen. Out of different fractions obtained by fractionation, the fraction with boiling point  $100 - 190^\circ\text{C}$  is selected and mixed with compressed hydrogen. This mixture is heated up to  $500^\circ\text{C}$  by passing through a heater. After compressing to about 25 atm. The mixture is passed through a series of three reactors each containing the  $(\text{Pt} - \text{Al}_2\text{O}_3)$  catalyst bed. The vapours need to be preheated, before passing from one reactor to another, because reforming process is endothermic. The products are separated into a liquid phase and a gas phase (consisting of  $\text{H}_2$  and  $\text{H}_2\text{S}$ ). The  $\text{H}_2\text{S}$  is derived from sulphur compounds in the feed. It can be removed by absorbing it in diethanolamine (DEA). This is done in  $\text{H}_2\text{S}$  scrubber. Part of  $\text{H}_2$  is recycled for removing S in feed stock as  $\text{H}_2\text{S}$  and remaining is used for other purposes like hydrogenation of alkenes and hydrocracking. By boiling, DEA can be regenerated and hence can again be used for scrubbing. The residue from the condenser is fractionated to remove the gases and higher boiling fractions.

The reformed or stabilized gasoline is also known as Plat-formates.

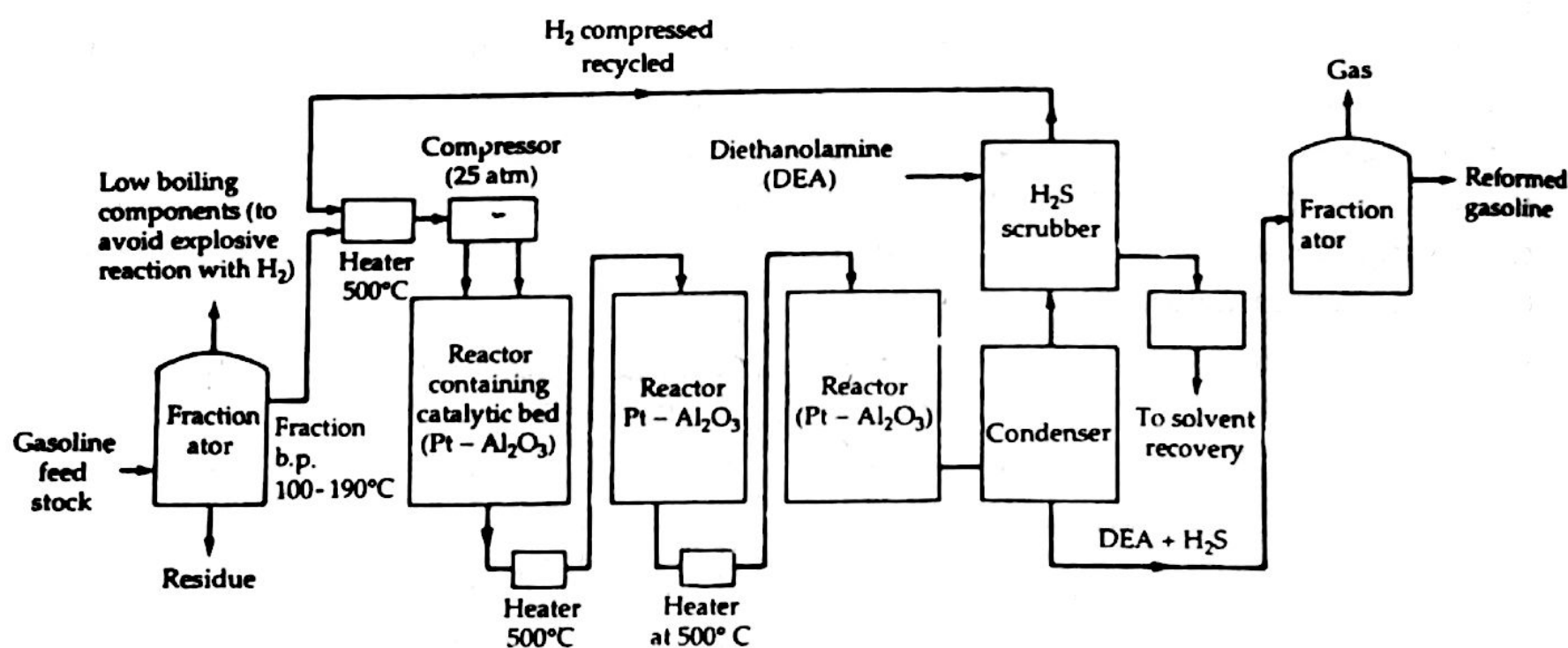
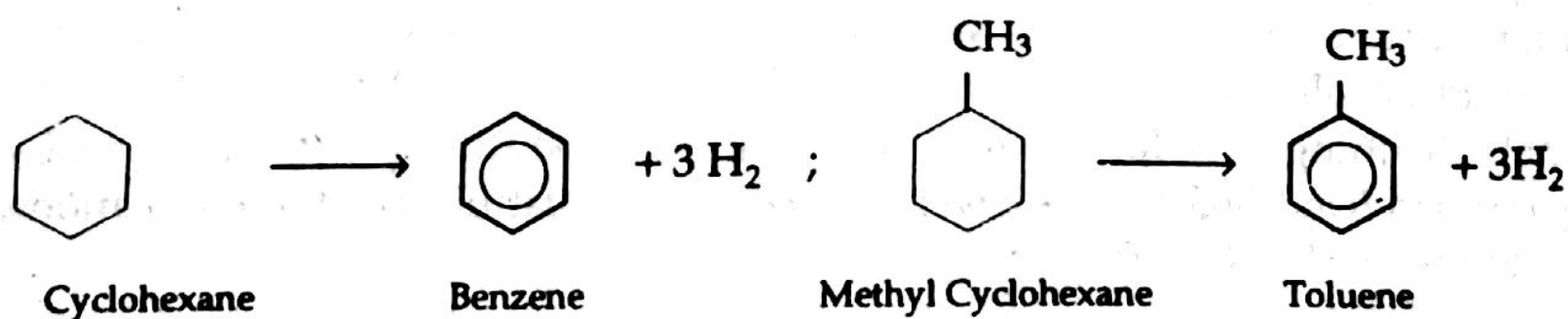
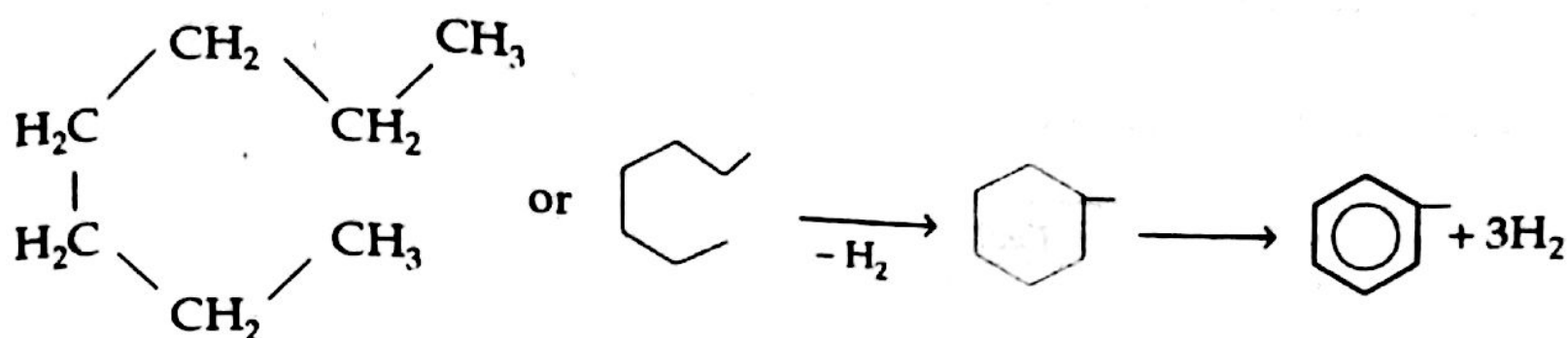
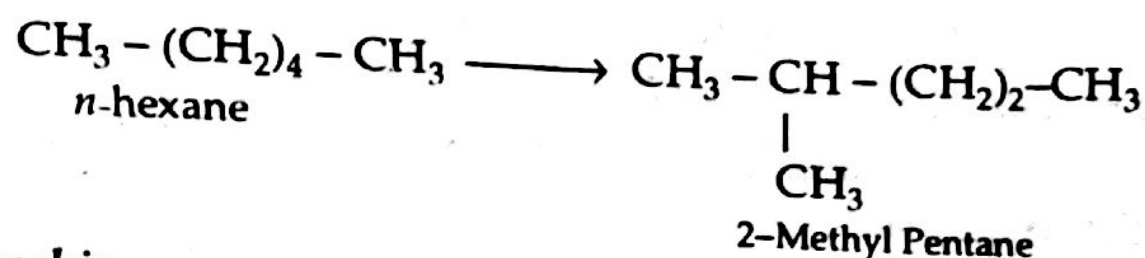
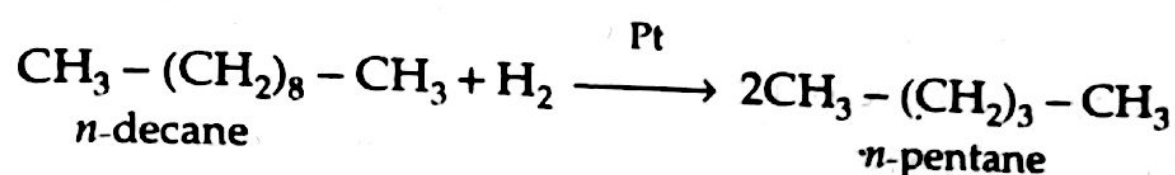


Fig. 22. Fixed-bed catalytic reforming process.

*The main reactions in the reforming process are :*

(i) **Dehydrogenation**



(ii) *Dehydrocyclization*(iii) *Isomerization*(iv) *Hydrocracking*

To summarize, the Octane number of a fuel may be improved by

- Blending : low octane petrol is blended with high octane compounds like alcohol e.g., power alcohol.
- The addition of anti-knock compounds like TEL.
- Reforming.

**22 AVIATION GASOLINE**

It is the gasoline which is used as a fuel in aeroplanes and combat planes. Different grades of aviation gasolines have different colours as it helps in easy identification :

GRADE of gasoline	73/80	91/96	100/130	115/145
COLOUR	Colourless	Blue	Green	Purple

Aviation gasoline is desired to be high octane fuels. For instance, the speed of an air plane using 87 octane fuel may be increased from 236 m.p.h. to 260 m.p.h., if 100 octane fuel is used.

The aviation gasoline is prepared by mixing alkylated branched paraffins with cracked gasoline containing unsaturated open chain hydrocarbons. This combination will obviously has high octane number so it will be more useful.

**23 POWER ALCOHOL**

Ethyl alcohol used for power generation *via* its use as a fuel for internal combustion engine, is called 'power alcohol'.

Ethyl alcohol is only used as an additive to motor fuel. Blends containing upto 25% of alcohol with petrol are used.



**Advantages of alcohol-blended petrol**

(1) Addition of alcohol to petrol increases its octane number. Hence, alcohol blended-petrol possesses better anti-knock properties.

<i>Fuel</i>	<i>Octane no.</i>
Alcohol	90
Petrol	60-70

(2) Alcohol-petrol blends have lesser starting difficulties.

**Disadvantages of alcohol-blended petrol**

1. Alcohol lowers the calorific value of petrol, because its calorific value is only two-third that of petrol.

2. Alcohol is easily oxidized to acids, hence may cause corrosion.

3. The ratio of flow of blend is to be increased to 1.56 times to that of pure petrol by altering the size of carburetor jet.

4. Since the alcohol-blended petrol requires less air than the pure gasoline, the air entering the cylinders is to be regulated either by modifying air inlet or by operating choke.

5. Because of its considerable surface tension, alcohol is difficult to atomize, particularly at low temperatures. Hence, specific arrangements for starting alcohol petrol blends in carburetor is to be provided.

**Note.** Absolute alcohol is 100%  $C_2H_5OH$  and Rectified spirit is 93-95%  $C_2H_5OH$ . Rectified spirit mixes well with petrol only in presence of benzene or ether. Hence, whenever it is used as power alcohol, either of the solvent must be used.

**Manufacture of alcohol from molasses**

The dark brown coloured mother liquor left after crystallisation of sucrose from concentrated sugar cane juice is known as molasses.

It contains about 50-60% can sugar (sucrose) plus invert sugar (glucose + fructose).

It forms an excellent and cheap raw material for the manufacture of alcohol in India, because the recovery of these sugars from molasses is not an economical process.

Molasses is converted into ethyl alcohol by the following steps :

(i) **Dilution.** Molasses is first of all diluted with water to get about 8-10% solution of sugar, because the high conc. of sugars is undesirable for the fermentation reaction.

(ii) **Addition of dilute sulphuric acid.** The diluted molasses is acidified with small amount of dil  $H_2SO_4$ . Dil  $H_2SO_4$  checks the growth of undesirable bacteria which would otherwise form lactic acid and acetic acid.

(iii) **Addition of ammonium salts.** To the above solution a small quantity of ammonium salt (ammonium sulphate and ammonium phosphate) is added, which acts as a food for the ferment and hence these are added only when molasses contain insufficient yeast food.

(iv) **Addition of yeast (Alcoholic fermentation).** Fermentation is the process in which complex organic substances are decomposed into simple compounds due to the activity of micro-organism (yeast or enzymes). The above solution of molasses





## 24 GASEOUS FUELS

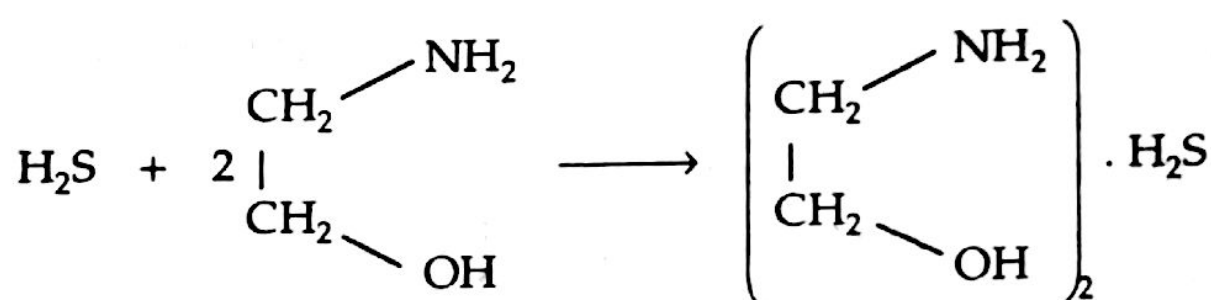
The most important gaseous fuels are Natural gas (1° fuel) and producer gas, water gas, carburetted water gas & coal gas (2° fuels). These are briefly discussed below :

### 24.1 Natural Gas

Natural gas is obtained from well dug in the oil-bearing regions. It is mainly composed of methane, ethane and other hydrocarbons. If lower hydrocarbons like methane and ethane are present, the natural gas is called dry or lean. If higher hydrocarbons are present along with methane, the natural gas is called wet or rich. It is also called 'Marsh gas' because it majorily contains methane. The average composition of natural gas is as follows :

Constituent	Methane	Ethane	Propane	Butane	Pentane, H <sub>2</sub> , CO, CO <sub>2</sub> and higher hydrocarbons.
Percentage	88.5%	5.5%	3.7%	1.8%	0.5%

"Sour" natural gas contains appreciable quantities of H<sub>2</sub>S which can be removed by scrubbing with mono ethanolamine :



On heating, H<sub>2</sub>S is liberated.

The calorific value of natural gas varies from 8,000 – 14,000 kcal/m<sup>3</sup>

#### Applications.

(a) As Natural gas can be conveyed over very large distances in pipelines, it is finding increasing use as a domestic and industrial fuel.

(b) It is also used as a raw material for

(i) the manufacture of carbon black and hydrogen which in turn are used as filler for rubber and ammonia synthesis respectively

(ii) Methanol, formaldehyde and other chemicals.

(c) Methane on microbiological fermentation gives synthetic proteins which are used as animal feed.

### 24.2 Compressed Natural Gas (CNG)

The natural gas compressed at very high pressure of about 1000 atmosphere is called compressed natural gas (CNG). It consists mainly of methane and it may contain small amounts of ethane, propane, butanes, pentanes, CO<sub>2</sub>, N<sub>2</sub> etc.

Concentration of methane in natural gas is 90% or even more. The calorific value of natural gas is 31400 – 37700 kJ/m<sup>3</sup>. A steel-cylinder containing 15 kg of CNG contains 20 m<sup>3</sup> of natural gas at 1 atm. pressure.



The use of CNG as a fuel for automobiles has reduced pollution in metropolitan cities to a considerable extent. This is mainly because of its complete combustion in CNG engine so there is minimum or nil possibility of release of unburnt carbon or CO in the atmosphere.

**Advantages of CNG :**

- (i) CNG is a much safer fuel. This is because the ignition temperature of CNG is higher than ignition temperature of diesel and gasoline,
- (ii) The operating cost of CNG fuel is much lower,
- (iii) Combustion of CNG leads to lesser CO emissions than gasoline.

**24.3 Liquefied Petroleum Gas (LPG)**

- LPG consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure, but can be liquefied easily under pressure.
- The main constituents of LPG are *n*-butane, iso-butane, butylene and propane, with little or no propylene and ethane.
- The main source of LPG is natural gas and from refining and cracking of petroleum.
- To help in the detection of gas leakage, a strong smelling substance "ethyl mercaptan ( $C_2H_5SH$ )" is added to the LPG gas cylinders which generally contain 14.2 kg of LPG. The calorific value of LPG is about 27,800 kcal/m<sup>3</sup>.
- Applications of LPG
  - (i) LPG is used as domestic fuel
  - (ii) LPG is used as industrial fuel, and
  - (iii) LPG is also used as motor fuel because it easily mixes with air and burns cleanly without residue and is knock-resistant.

**Advantages of LPG over gaseous fuel :**

- (i) The calorific value of LPG is roughly 3 times that of natural gas and 7 times that of coal gas.
- (ii) Portability in steel cylinder/containers, which makes its use possible in remote and isolated places.
- (iii) As it is free from CO so is comparatively less of health hazard, even in case of leakage.
- (iv) Flexibility and easy control.
- (v) Cleanliness in storage, handling and use.

**Advantages of LPG over gasoline as a motor fuel :**

- (i) Use of LPG is more economical than gasoline.
- (ii) LPG is highly knock resistant.
- (iii) LPG gives better manifold distribution and it mixes easily with air.
- (iv) LPG burns cleanly, residue and oil contamination is small.

**Disadvantages of LPG over gasoline as a motor fuel :**

- (i) LPG is suitable only for engines which work under high compression ratios.

- (ii) Detection of leakage is not easy because of faint odour,
- (iii) Requires high pressure for handling.
- (v) Its octane number is also low.

#### 24.4 Producer Gas

It is essentially a mixture of carbon monoxide (combustible gas) and nitrogen (non-combustible gas). It is cheap, clean and easily preparable gas.

It is insoluble in water and is poisonous in nature. Its calorific value is about  $900 - 1300 \text{ kcal/m}^3$

*Composition.* The average composition of producer gas is :

	Combustible gases		Non-combustible gases	
Constituent	CO	H <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
Percentage	22 – 30%	8 – 12%	52 – 55%	3%

*Production.* It is prepared by passing a mixture of air and little steam (about 0.35 kg/kg of coal) over a bed of red hot coal or coke in 'gas producer'. Gas producer is a special reactor consisting of a steel vessel, about 3 m in dia and 4 m in height. The vessel is lined from inside with refractory bricks because the coal or coke bed need to be maintained at about  $1100^\circ\text{C}$ . The gas producer has inlet for passing air and steam and outlet at the base for the exit for the ash formed. It is also provided with a cup and cone feeder at the top and a side opening for producer gas exist.

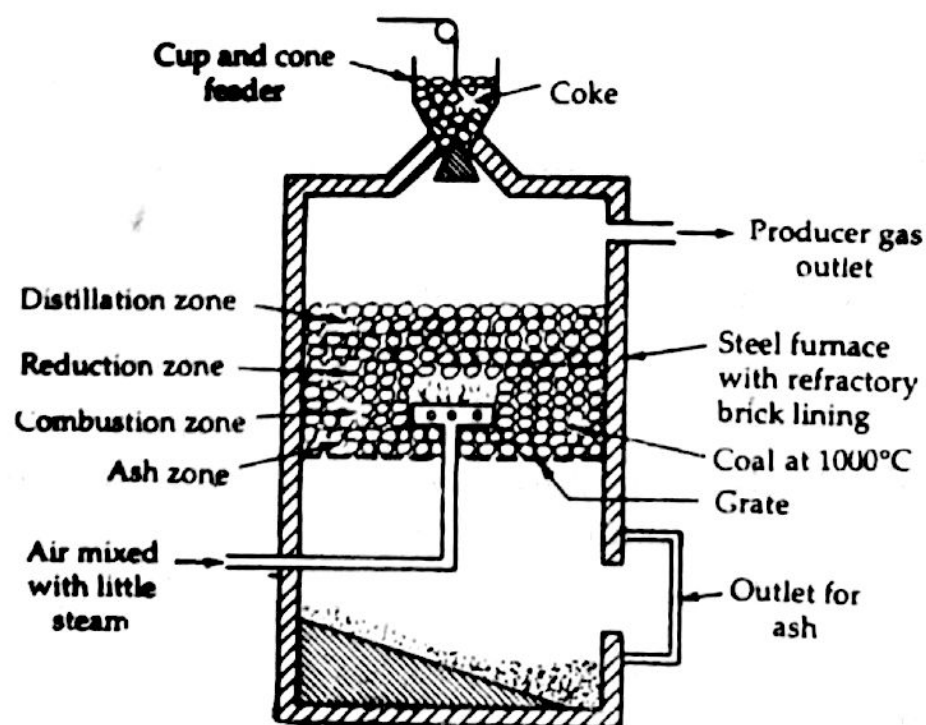
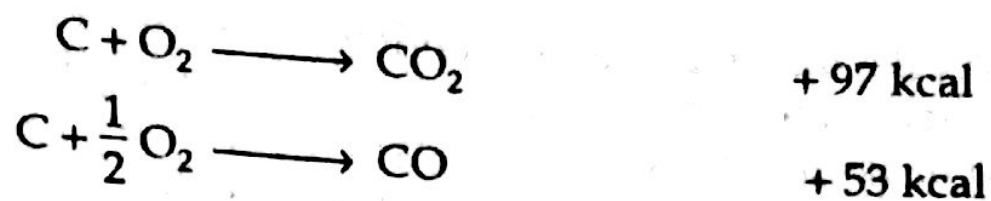


Fig. 23. Gas producer for the manufacture of producer gas.

When a mixture of air and steam is passed over red hot coke or coal bed at about  $1100^\circ\text{C}$  in gas producer, the following reactions take place in different zones of the fuel bed :

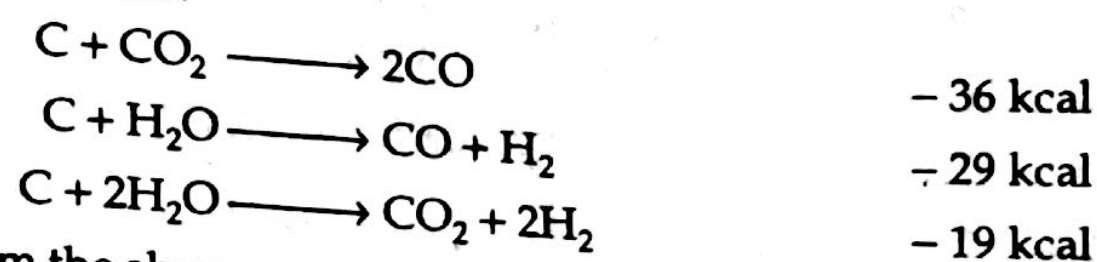
(a) *Ash zone.* As the name indicates, it mainly consists of ash. It is about 0.8 m thick and is the lowest zone. The grate of the producer plant is protected from the intense heat of combustion by ash. As air and steam is passed through this zone, their temperature is increased.

(b) *Combustion zone or oxidation zone.* In this zone, the carbon of the coal or coke, burns in the presence of air and gets oxidised to CO and CO<sub>2</sub>.



The temperature of this zone is about 1100°C.

(c) *Reduction zone.* This is the middle zone of gas producer. Here the steam and CO<sub>2</sub> (produced in the combustion zone) moves up through the red hot fuel bed and liberates free hydrogen and CO.



As can be seen from the above equations that these reactions are endothermic, so the temperature in the reduction zone falls to about 1000°C. If these reactions don't occur, the temperature further rises and this may fuse the ash and refractory lining. Hence, air mixed with little steam is used.

(d) *Distillation zone.* This is the region in the upper part of the fuel bed. In this zone, outgoing gases give their sensible heat to the down coming coal. This along with heat radiated from the reduction zone helps to distill the fuel, thereby volatile matter of coal is removed and comes out with outgoing gas.

#### Applications.

(a) Producer gas is used in many metallurgical processes as a reducing agent.

(b) It is also used as a fuel for heating open-hearth furnaces, muffle furnaces and retorts used in coke and coal gas manufacture.

### 24.5 Water Gas

It is essentially a mixture of carbon monoxide and hydrogen (combustible gases) with a little carbon dioxide and nitrogen (noncombustible gases). It is non luminous and burns with a blue flame. Its calorific value is about 2800 kcal/m<sup>3</sup>

*Composition.* The average composition of water gas is :

Constituent	Combustible gases		Non-combustible gases	
	CO	H <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
Percentage	41%	51%	4%	4%

*Production.* It is prepared by passing steam and little air alternatively over a bed of red hot coal or coke in a reactor. The reactor consists of a steel vessel, about 3 m in dia and 4 m in height. The vessel is lined from inside with refractory bricks because the coal or coke bed need to be maintained at about 900 to 1000°C. The reactor is provided with separate inlet pipes for passing air and steam. It is also provided with outlet at the base for the exit for the ash formed. There is cup and cone feeder at the top and an opening near the top for the exist of water gas.

First steam is passed over red hot coke or coal maintained at about 900 – 1000°C the carbon of coal or coke reacts with steam to form CO and H<sub>2</sub>, according to following equation :





As the above reaction is endothermic, the temperature of the bed falls. It is necessary to temporarily cut off the steam supply in order to raise the temperature of bed to about 1000°C. Air is blown in, when the oxygen of air reacts with carbon to form carbon-dioxide and carbon-monoxide

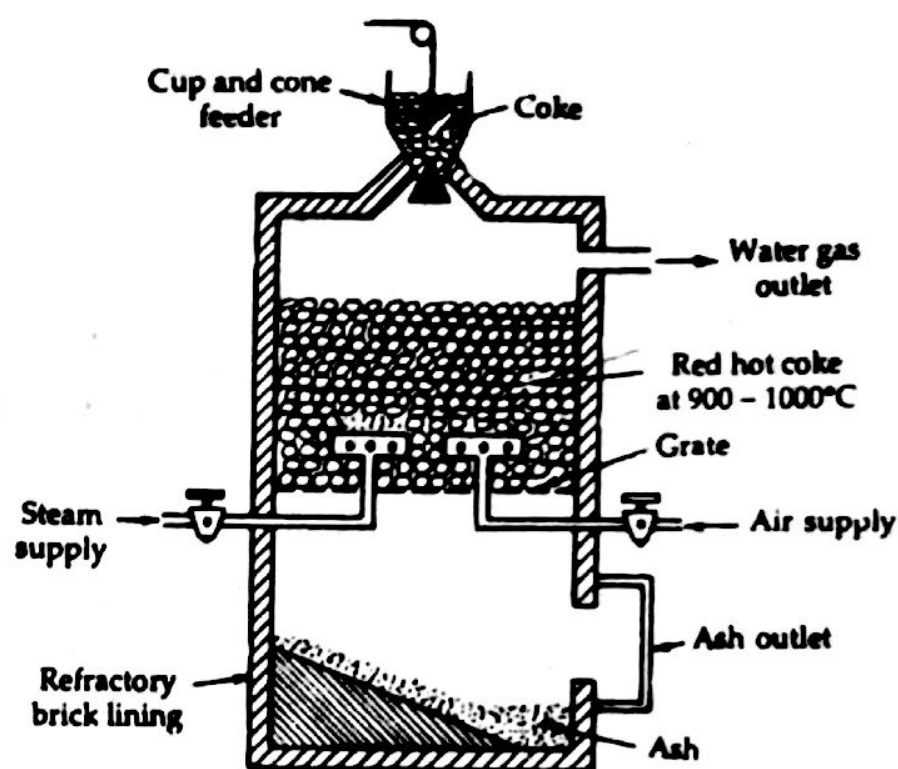
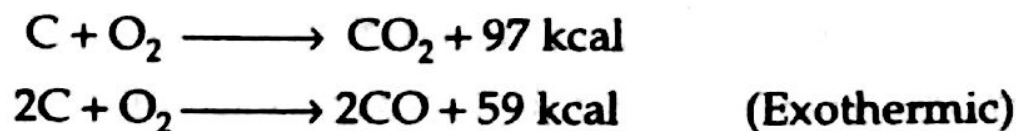


Fig. 24. Water gas production.

The above two exothermic reactions again raise the temperature of bed to about 1000°C. So, in order to maintain the temperature of bed, blow of steam and air has to be repeated alternately.

*Applications.* Water gas is used

- (a) as a source of hydrogen gas ;
- (b) as a fuel gas ;
- (c) as a raw material for Fischer-tropsch process for the manufacture of synthetic petrol ;
- (d) as an illuminating gas.

#### 24.6 Carburetted Water Gas

Cracking of crude oil also generates some gaseous hydrocarbons, and if the later are mixed with water gas, calorific value of water gas increases. Hence carburetted water gas is a mixture of water gas and gaseous hydrocarbons.

*Composition.*

Composition	H <sub>2</sub>	CO	Saturated and Unsaturated hydrocarbons	N <sub>2</sub> + CO <sub>2</sub>
Percentage	35%	25%	35%	5%

Its calorific value is about 4500 kcal/m<sup>3</sup>.

*Applications.* It is used for illumination and heating purposes.

#### 24.7 Coal Gas

Coal gas is lighter than air and is colourless gas. It has a characteristic odour and burns with a smoky flame. Its *average composition* is :

Constituent	H <sub>2</sub>	CH <sub>4</sub>	CO	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	N <sub>2</sub>	CO <sub>2</sub>	Rest
Percentage	40%	32%	7%	2%	3%	4%	1%	4%

The calorific value of coal gas is about  $4,900 \text{ kcal/m}^3$ .

**Production.** When coal is carbonized (heated in the absence of air) at about  $1300^\circ\text{C}$  in either gas making retorts or coke ovens, coal gas is obtained.

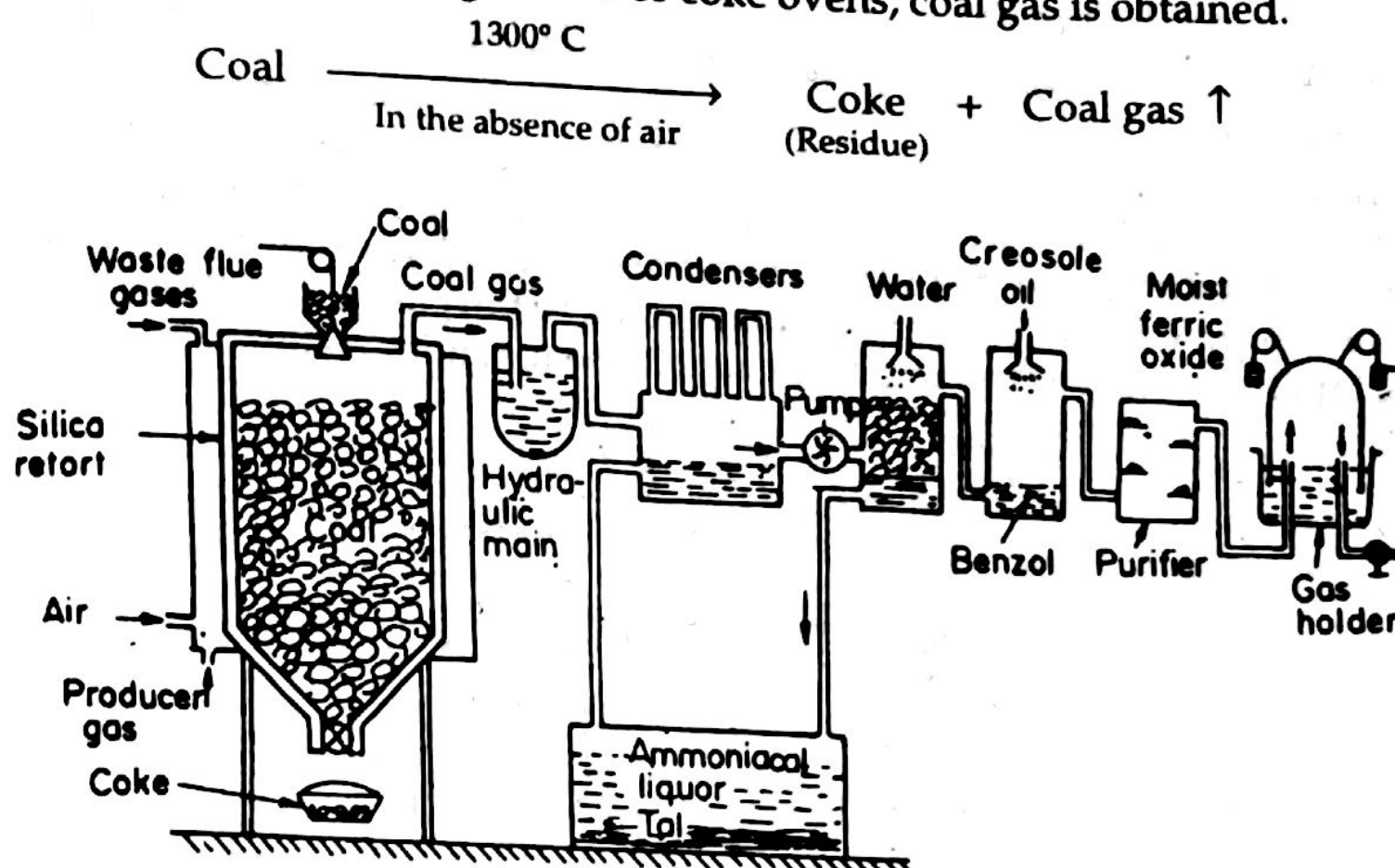
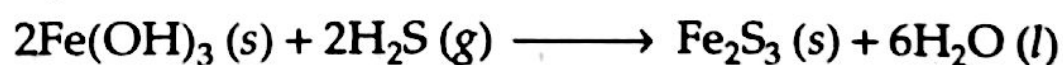


Fig. 25. Manufacture of coal gas.

With the help of cup and cone feeder, powdered coal is fed from the top into the large, vertical, silica retorts. The retorts are heated externally (by burning a mixture of producer gas and air) to about  $1300^\circ\text{C}$ . The coal gas thus obtained is impure. It contains number of valuable impurities like tar, ammonia, benzol, naphthalene and hydrogen sulphide. The by-products are removed from the coal gas to improve the quality of gas. These by-products also have their utility value. The gas is first scrubbed by passing through a hydraulic main, which acts as a water seal. The scrubbing removes some tar and water soluble products such as ammonia. Much of the tar is then removed by cooling the gas in condenser (a huge water cooled heat exchanger). Ammonia (and any remaining tar) can be removed by scrubbing with water in a scrubber. Benzol, naphthalene, etc., are removed by scrubbing with cresote oil. Hydrogen sulphide is removed by passing the gas over moist ferric oxide,



The purified coal gas is finally stored over water in gas holders.

**Applications.** Coal gas is used as (a) a fuel ; (b) for providing reducing atmosphere in many metallurgical operations ; and (c) illuminant in cities and towns.

## 24.8 Oil gas

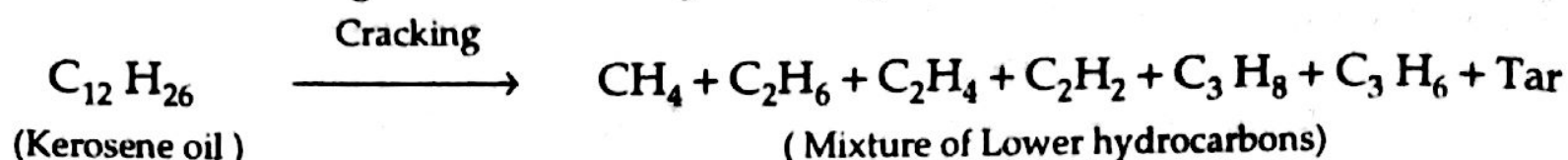
Oil gas has characteristic golden colour, it burns with a smoky flame.

The approximate composition of the oil gas is :

Constituent	Methane ( $\text{CH}_4$ )	Hydrogen ( $\text{H}_2$ )	Carbon monoxide ( $\text{CO}$ )	Carbon dioxide ( $\text{CO}_2$ )
Percentage	25 – 30%	50 – 55%	10 – 15%	3%

The calorific value of oil gas is about 4500 – 5400 kcal/m<sup>3</sup>.

*Production.* Oil gas is obtained by cracking of kerosene oil.



Cracking of kerosene oil is done in strong cast iron retort, enclosed in a coal-fired furnace. At the mouth of the retort, a bonnet is fitted through a molten lead seal. The other end of the bonnet is connected to a hydraulic main, through a water seal. A pipe from the hydraulic main leads to the gas holder. This pipe has a testing tap. From where the samples of gas can be taken for testing.

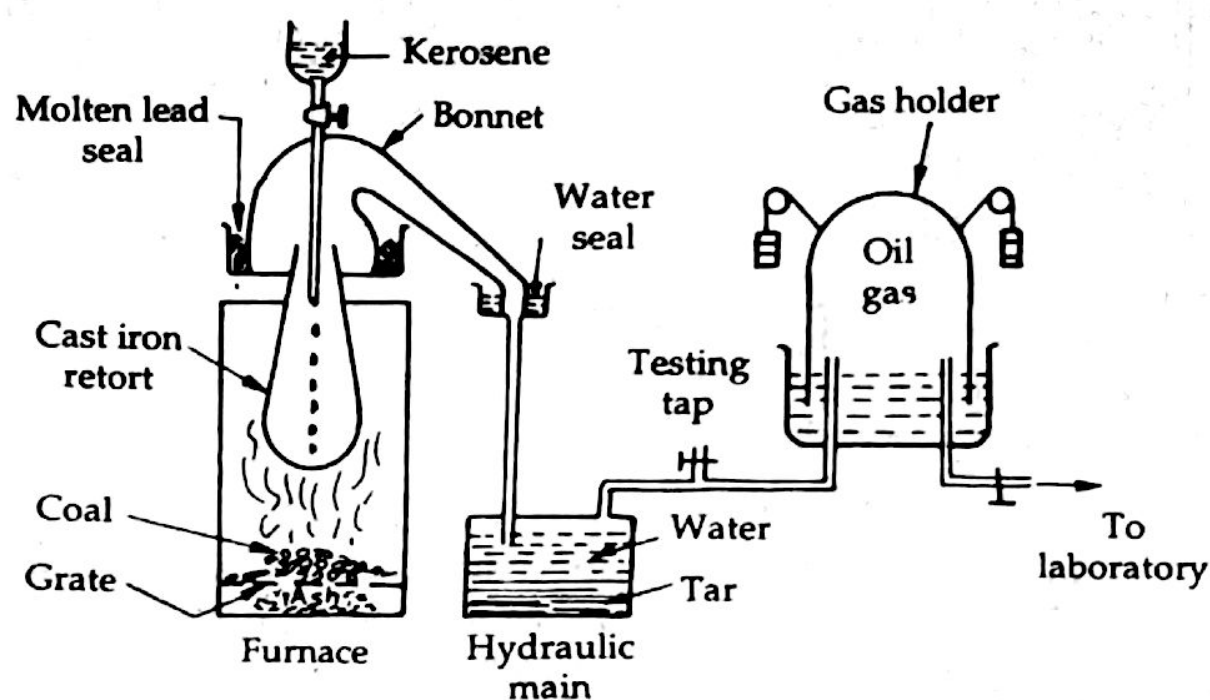


Fig. 26. Laboratory preparation of oil gas.

The proper cracking of the oil is estimated from the colour of the gas. A good oil gas should have a golden colour. Finally, the gas is stored over water in gas holders. Yield of the gas is about 40 to 50%. From the gas holders, gas is conveyed to laboratory through pipes, whenever required.

*Applications.* Oil gas is used as laboratory gas. It is also used to improve the calorific value of water gas and the mixture of the two gases is called carburetted water gas.

## 24.9 Bio gas

The cheapest and most easily available bio-gas is gobar gas. It consists mainly of methane. It burns with a blue flame and its average calorific value is about 5300 kcal/m<sup>3</sup>.

*Composition.* The composition of gobar gas is :

Constituent	Methane (CH <sub>4</sub> )	Hydrogen (H <sub>2</sub> )	Carbon dioxide (CO <sub>2</sub> )	Nitrogen (N <sub>2</sub> )
Percentage	55%	7.4%	35%	2.6%

*Production.* Gobar gas is manufactured in gobar gas plant, which consists of (i) a 'well' constructed of masonry work (also known as 'digester'). The digester is usually built below the ground level, (ii) a 'gas holder' which covers digester and made up of weld steel sheets and (iii) a 'pipeline', 10 cm in diameter. See figure 27.



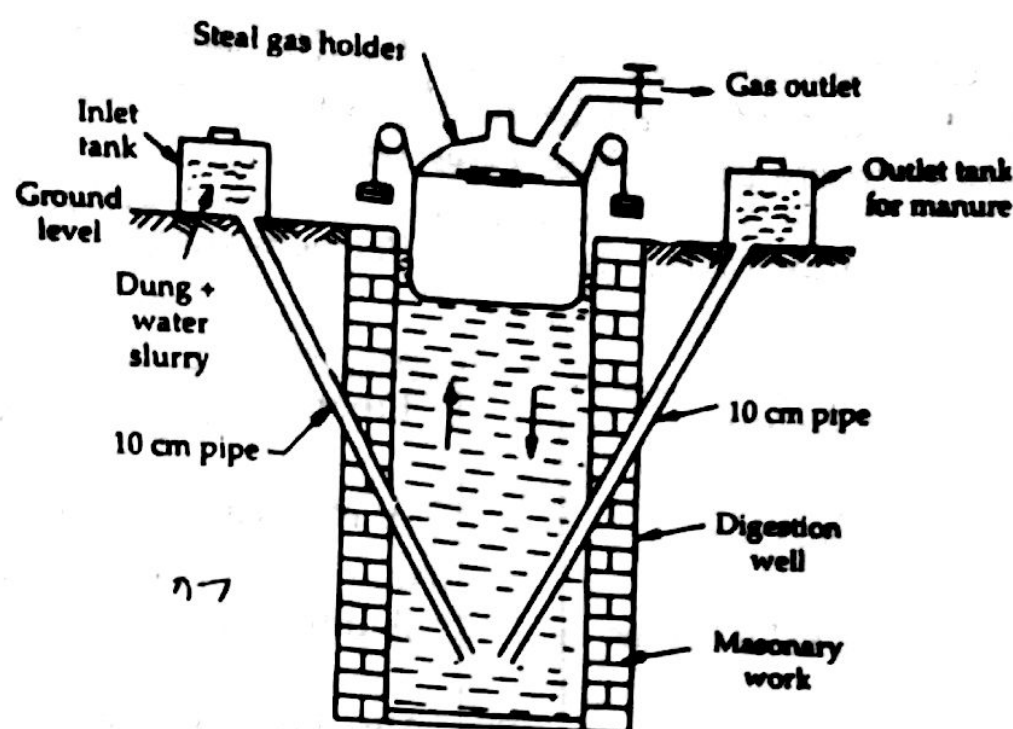


Fig. 27. Gobar gas plant.

Cattle dung in the form of slurry (made by mixing equal parts of water) is poured in digester. Anaerobic bacteria's present in the dung digest this slurry in a process called anaerobic fermentation. The optimum temperature for this fermentation is  $34 - 48^{\circ}\text{C}$ . The gas generated, due to continuous decay, is mostly methane and is collected in gas holder. It is interesting to note that in addition to cattle dung gobar gas plant can also digest human refuse, poultry, sweeps etc.

#### Advantages :

1. Heat generated by direct burning, 1 kg of dry cattle dung is 23.4 kcal but if the same amount of cattle dung is converted first into gobar gas, [160 l gas per kg dung], it can supply 188 kcal of heat ;
2. Gobar gas does not contain poisonous gas, CO as an ingredient ;
3. Gobar gas is free from smoke, dust, dirt etc., hence by its use, environment and utensil remain comparatively clean ;
4. By producing gobar gas, we in fact are optimally utilizing waste ;
5. It can provide the flame temperature of  $540^{\circ}\text{C}$ , with proper burners.

**Limitation.** Gobar gas should be used within 10 metres of the gobar gas plant.

#### Applications :

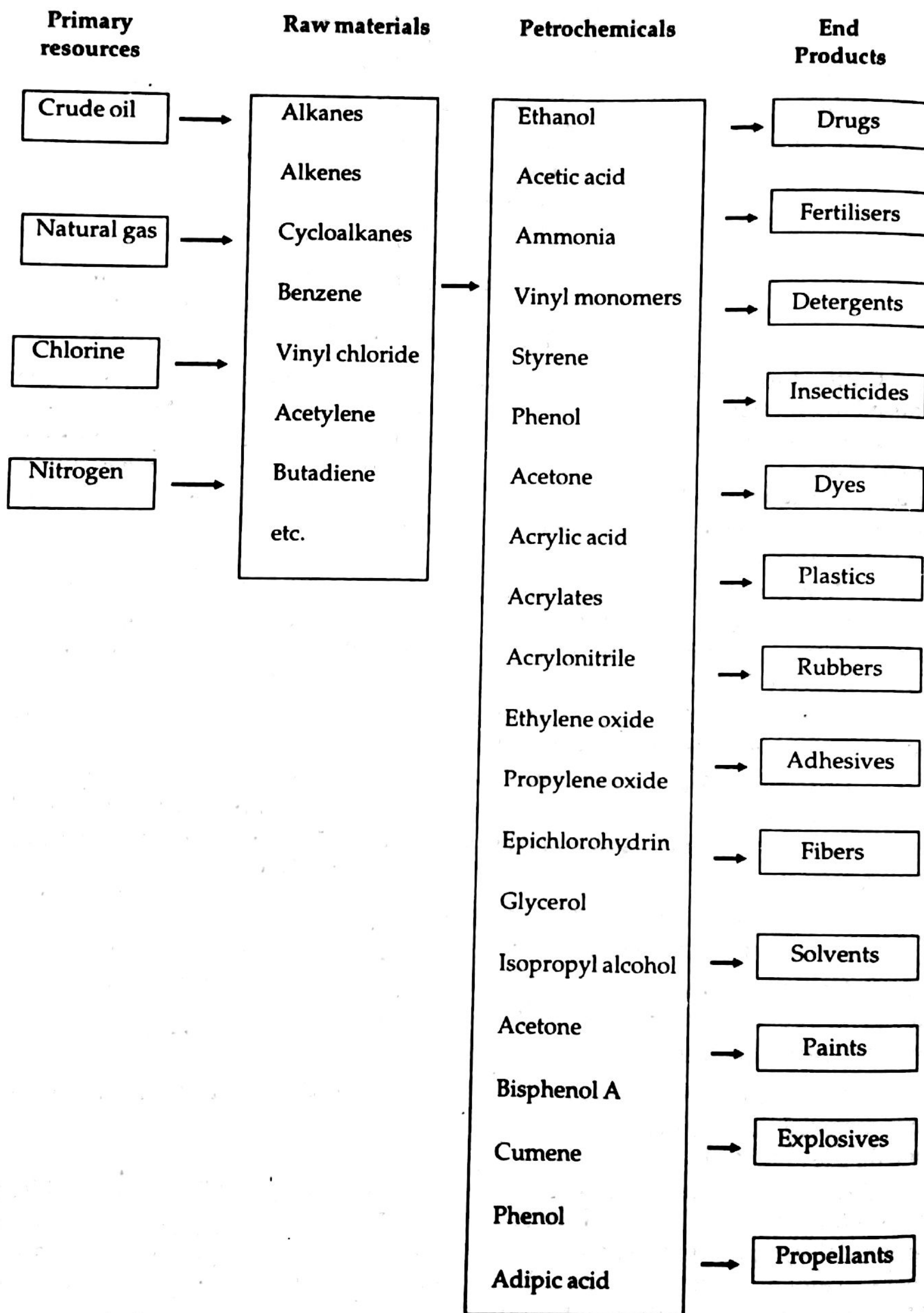
1. It is used as domestic fuel in many villages ;
2. It is also used for lighting and power purposes ;
3. Gobar gas also gives simultaneously excellent yield of good manure which has 2% nitrogen content as against 0.75% in farm yard manure.

## 25 PETROCHEMICALS

*Petrochemicals* are the chemicals and chemical products which are made from raw materials derived from petroleum and its fractions. They are also known as petroleum chemicals.

Alkanes, Alkenes, cycloalkanes, benzene and its homologues are derived from petroleum and its fractions. These are used as *raw materials* for the manufacture of industrially important *chemicals* such as ethanol, acetic acid, ammonia, vinyl monomers, acetone, phenol, acrylonitrile, styrene etc. These chemicals find extensive applications in the *industries* for production of solvents, explosives, drugs, paints, dyes, fibers, fertilizers, plastics, rubbers, adhesives, insecticides, detergents etc.

This, in turn, result in tremendous demand for the basic raw materials. This is the reason for the installation of petrochemical plants of large capacities. This is how the modern era of petrochemicals has dawned.



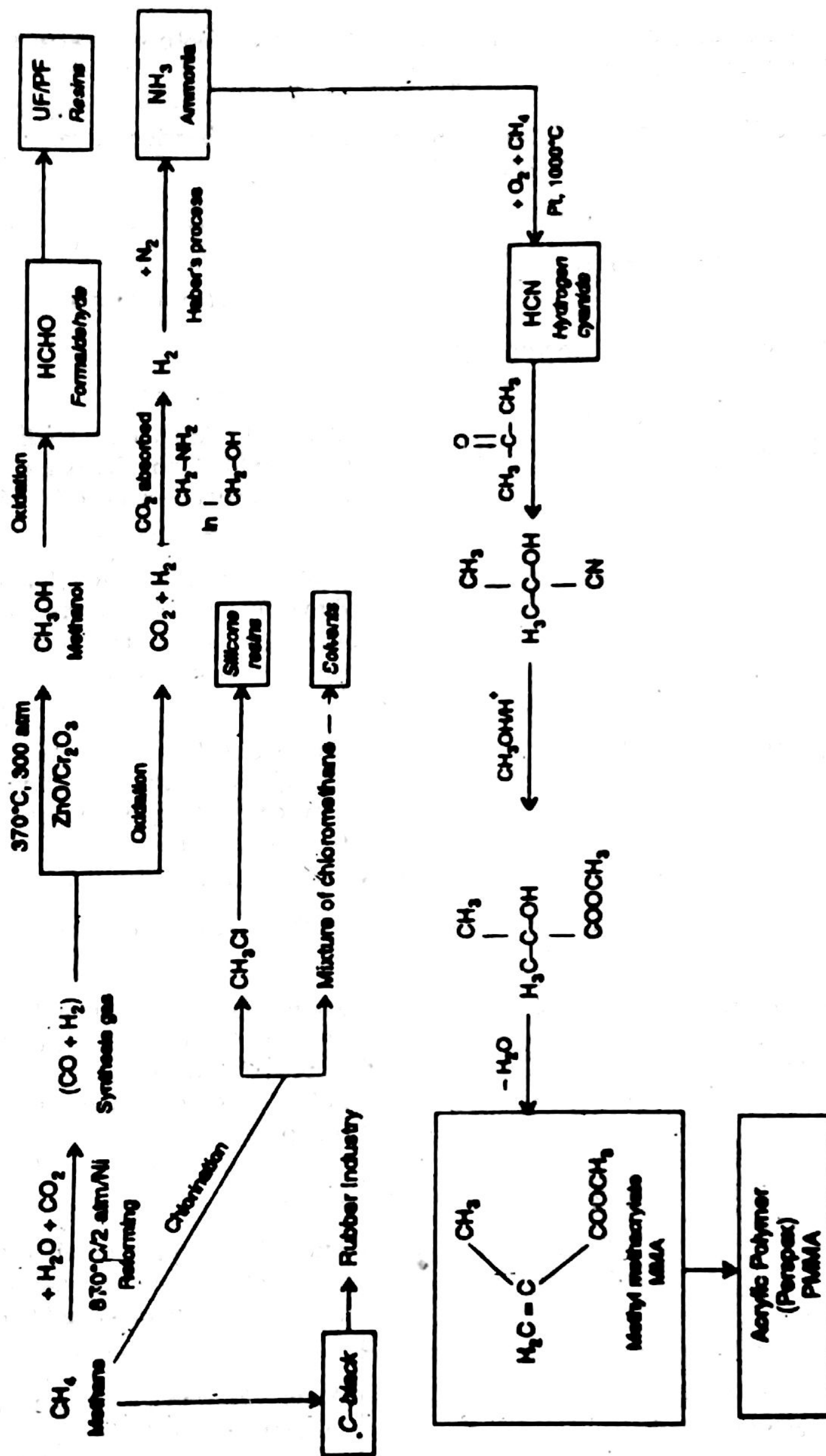
**Fig. 27.** Production of industrially useful products from petrochemicals which in turn are derived from petroleum and its fractions.

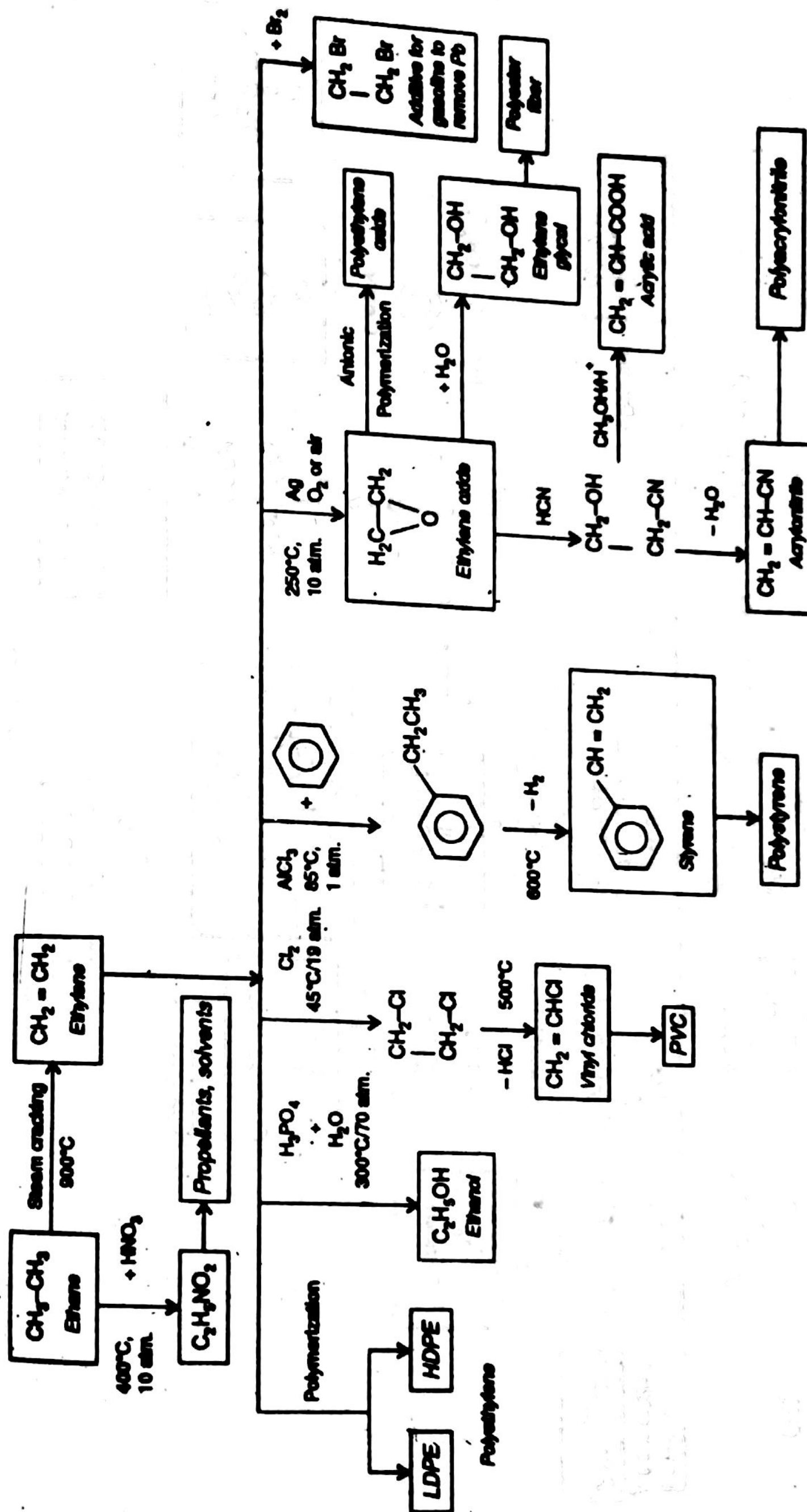
The primary and secondary raw materials for the manufacture of petrochemicals are summarized in table 12.

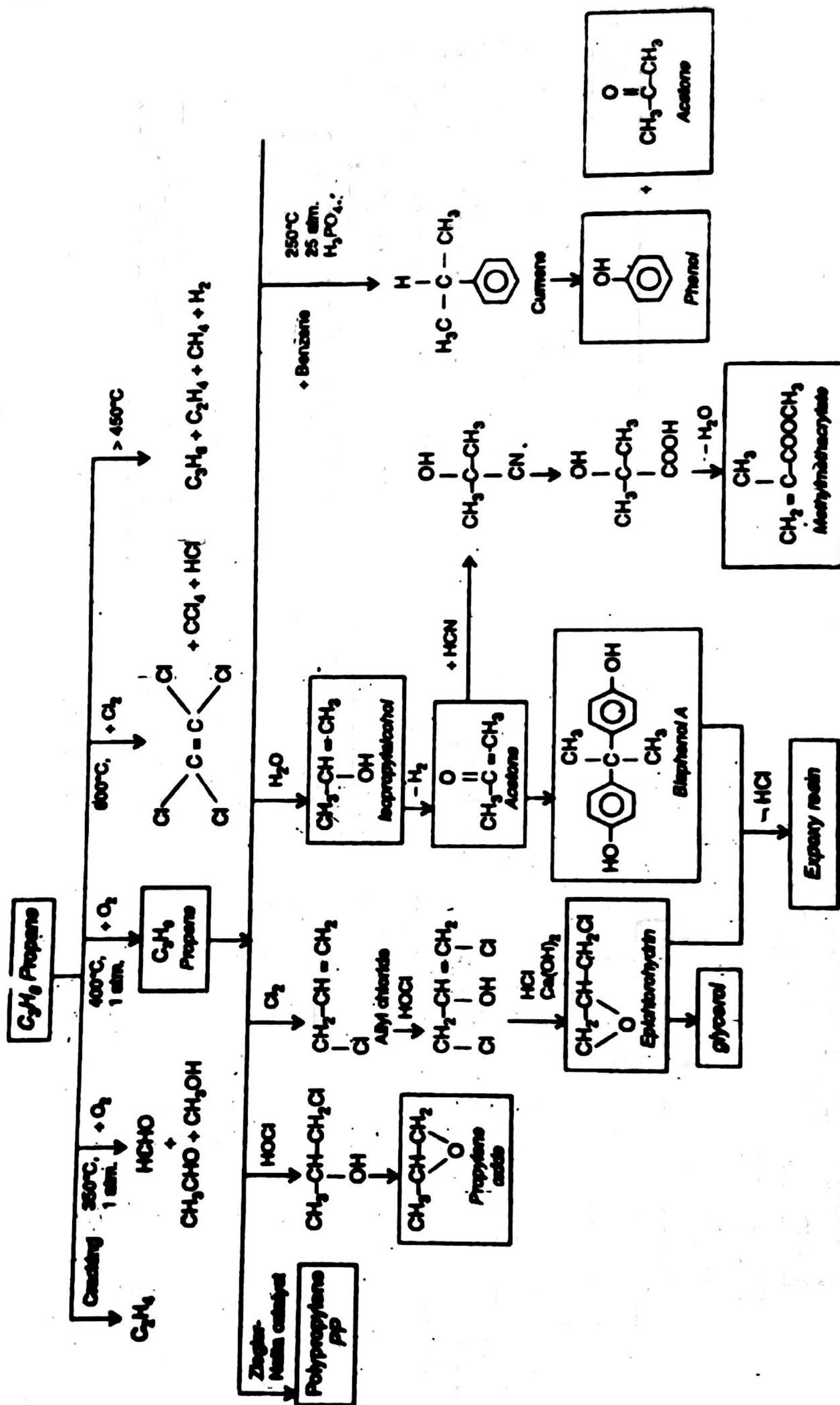
**Table 12 : Primary and Secondary raw-materials from Petroleum and Corresponding Petrochemicals**

Raw-materials		Petrochemicals
Primary	Secondary	
Natural gas (from refineries and oil fields)	Methane	Methanol, Ammonia, Hydrogen Cyanide, Methylmethacrylate (Refer C <sub>1</sub> stream on Page AC.149)
	Acetylene	Acetaldehyde, Acrylonitrile, Ethylene glycol, acrylic acid, acrylates, vinyl monomers and acrylic monomers etc.
Refinery gases (from crude-oil fractionation, cracking and reforming processes)	Ethene	Ethylene oxide, Acrylonitrile, Ethylene glycol, acrylic acid, acrylates, vinyl chloride, styrene, Ethanol (Refer C <sub>2</sub> stream on Page AC.150)
	Acetylene, Ethene	As Discussed above
Liquid hydrocarbons (Naphtha fraction obtained from the distillation of crude oil)	Propylene	Propylene oxide, Epichlorohydrin, glycerol, Acrylic acid, acrylonitrile, isopropyl alcohol, acetone, bisphenol A, Methylmethacrylates, cumene, phenol (Refer C <sub>4</sub> stream on Page AC.151)
	Butylenes and butadiene	Butanols, Ethyl methyl ketone, Ethyl butyl ketone, isooctane etc. (Refer C <sub>4</sub> stream on Page AC.152)
C <sub>6</sub> - C <sub>8</sub> fraction from petroleum fractionation	Benzene	Alkyl benzene, Adipic acid, Hexamethylene diamine. (Refer C <sub>5</sub> stream on Page AC.153)
	Toluene	Benzoic acid, caprolactum

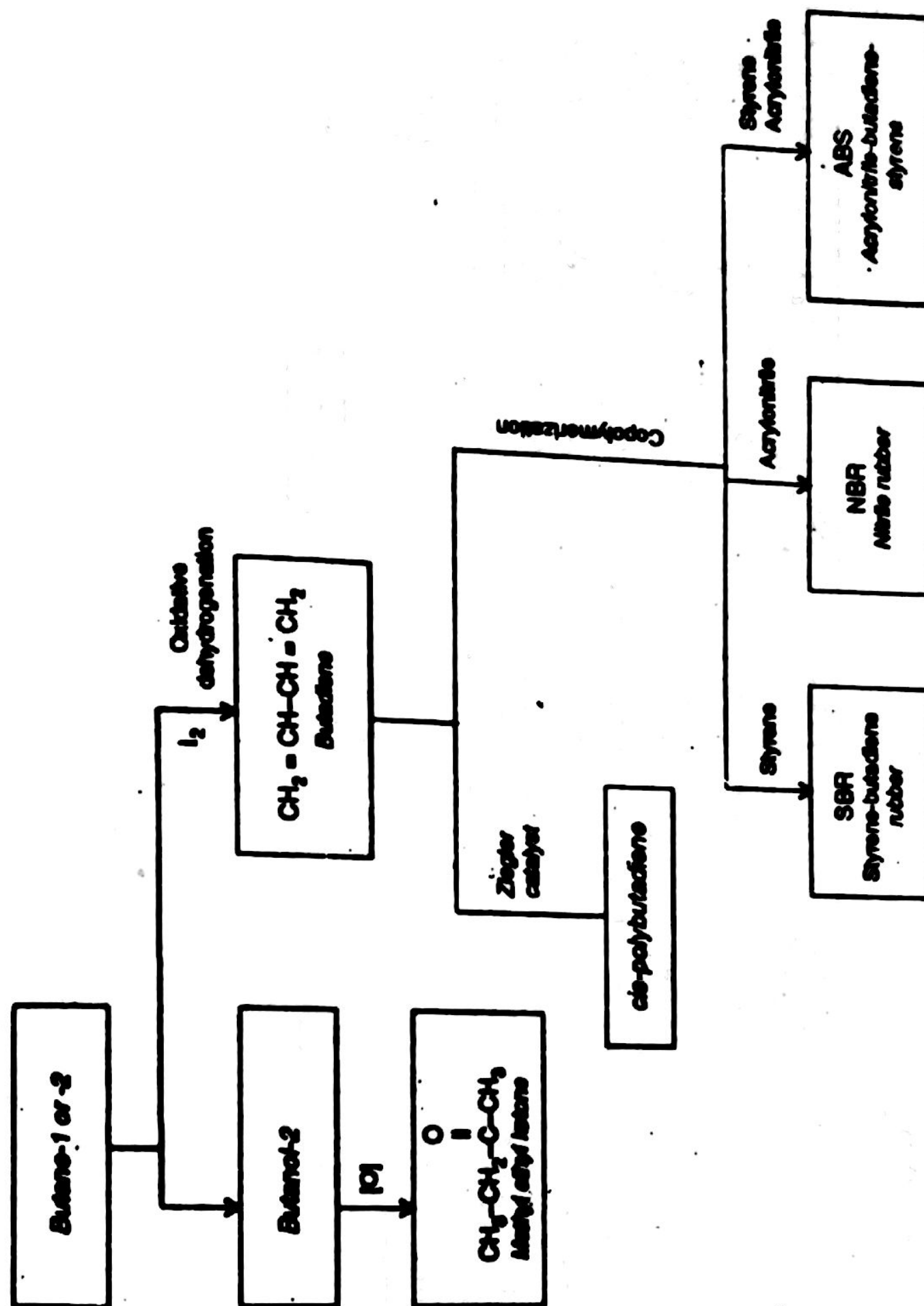


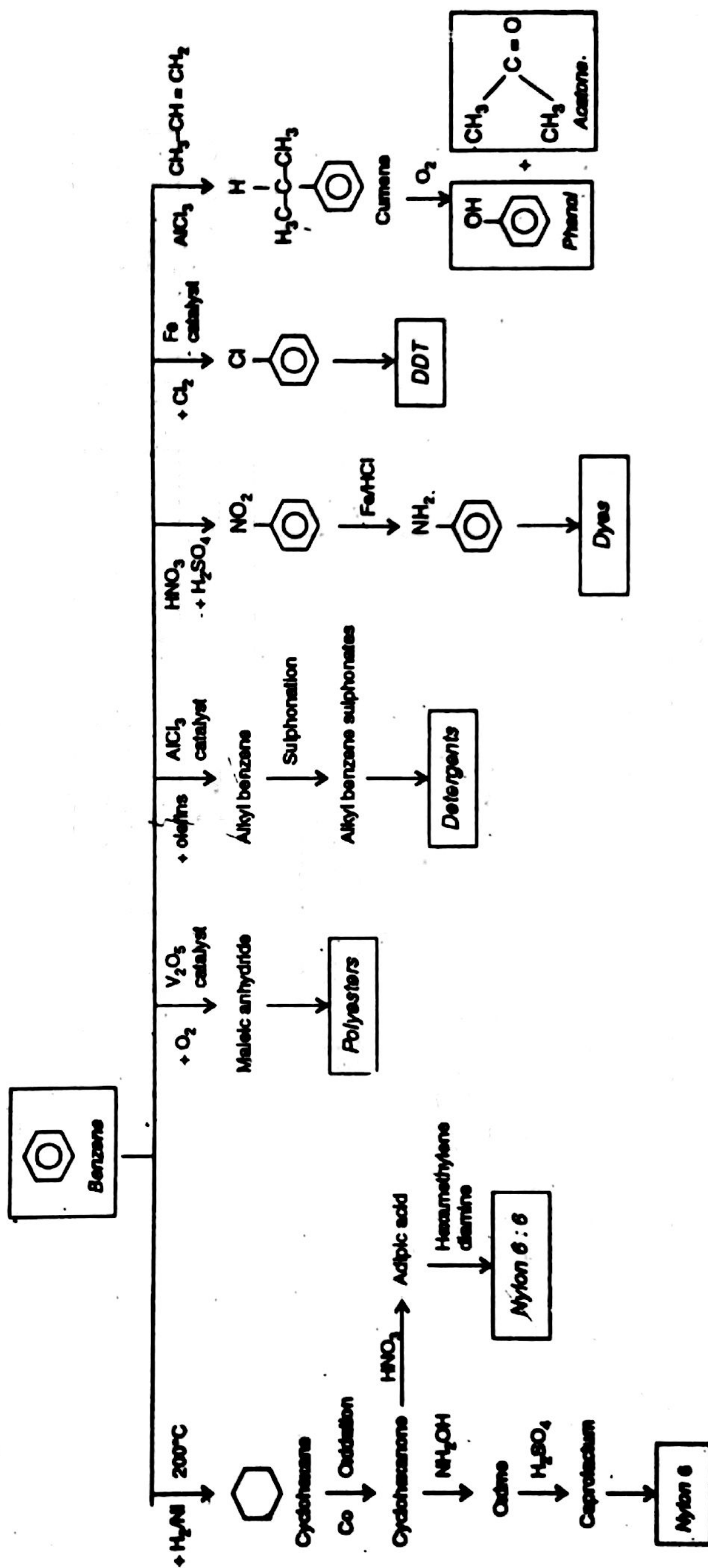
Figure :  $C_1$  Stream.

Figure :  $C_2$  stream.

Figure : C<sub>3</sub> stream.



Figure : C<sub>4</sub> stream.



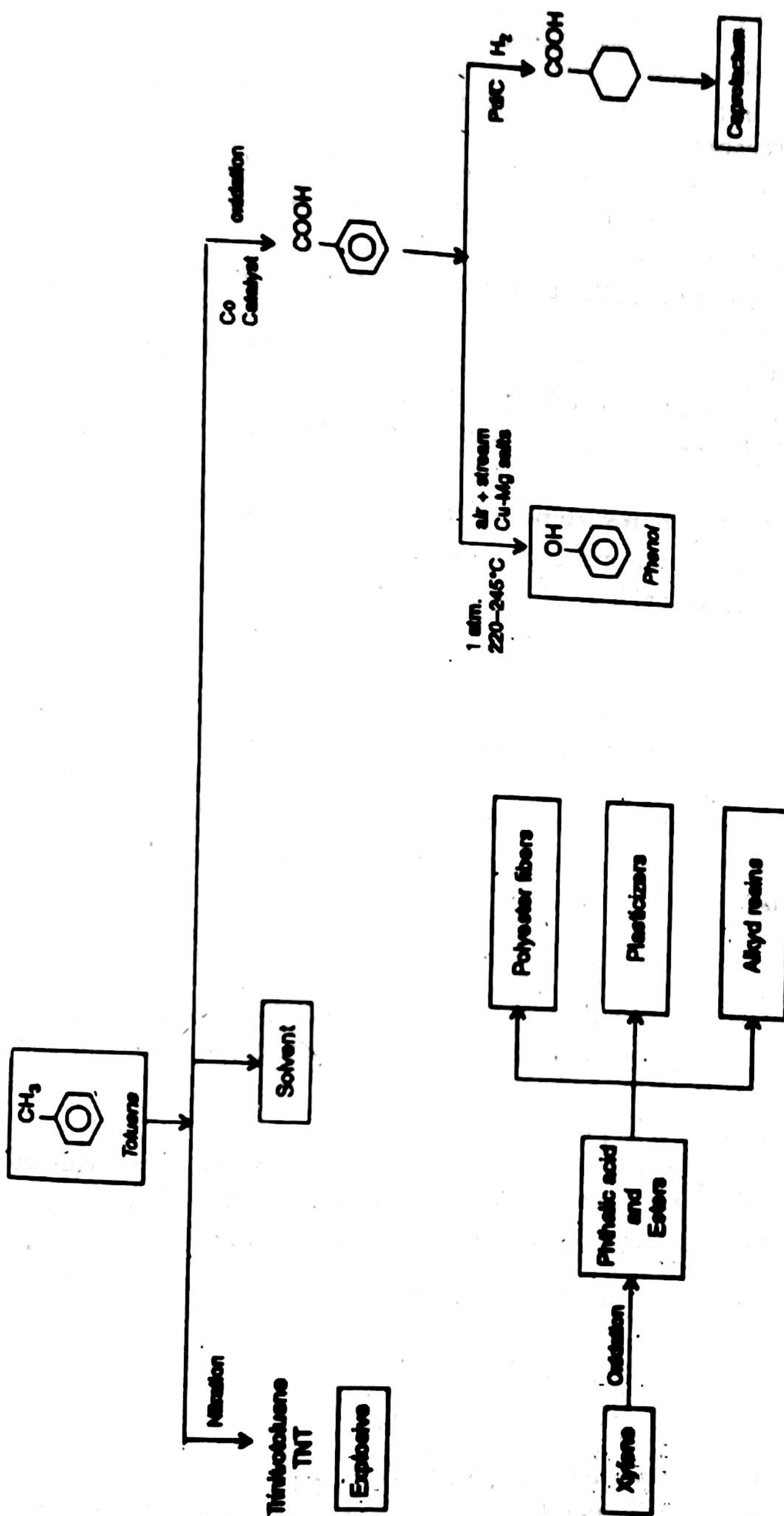


Figure : C<sub>8</sub>-C<sub>9</sub> stream.



**SOLVED QUESTIONS**

**Q. 1. Gasoline containing tetraethyl lead (TEL) is used in internal combustion engines. Give reasons.**

**Ans.** TEL gives rise to Pb and PbO during combustion. These particles act as free-radical chain inhibitors as they arrest the propagation of the explosive chain reactions responsible for knocking.

**Q. 2. Why small amount of ethylene dibromide or ethyl bromide along with TEL is used in I.C. engines ?**

**Ans.** Pb and PbO<sub>2</sub> from TEL decreases engine life hence they must be removed along with exhaust gases by adding ethylene dibromide.

(Pb, PbO<sub>2</sub> + C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub> → PbBr<sub>2</sub>). Because PbBr<sub>2</sub> formed is volatile it escapes into atmosphere.

**Q. 3. Mention the different varieties of coal formed inside the earth.**

**Ans.** Coal varieties : Peat, lignite, bituminous and anthracite.

**Q. 4. Which variety of coal is used in metallurgy ? Give also its approximate calorific value.**

**Ans.** Coal : Anthracite

Calorific value : 8650 to 8700 kCal/kg.

**Q. 5. Differentiate between caking coals and coking coals.**

**Ans.** Those coals which on heating in the absence of air become soft, plastic and fuse together to form large coherent masses are known as *caking coals*.

While those coals which on heating give porous, hard and strong residues are known as *coking coals*.

It is to be noted that only coking coals are useful for metallurgical purposes.

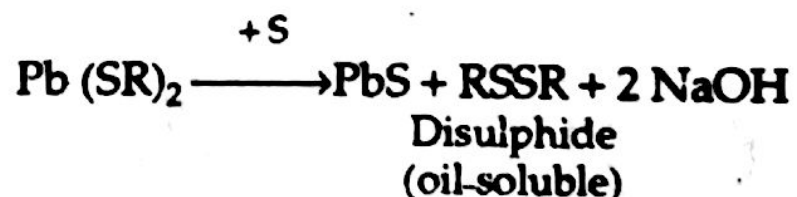
**Q. 6. What is synthetic petrol ?**

**Ans.** Synthetic petrol is one which is synthesised either from finely powdered coal and heavy oil or from polymerization of low molecular mass olefins and alkanes.

**Q. 7. What is sweetening of petrol ?**

**Ans.** Sweetening of petrol means treatment of petrol (or gasoline) with an alkaline solution of sodium plumbite with controlled addition of sulphur.

It is done for removing harmful sulphur compounds from petrol.



**Q. 8. Give the condition when GCV = NCV.**

**Ans.** If the fuel does not contain hydrogen (e.g., pure carbon, sulphur, etc.), then GCV = NCV.

**Q. 9. What are fossil fuels and how are they formed ?**

**Ans.** Coal, petroleum and natural gas are examples of the fossil fuels. They are formed from dead animals and plants, whose remains are subjected to heat and high pressures.

**Q. 10. What energy conversion takes place when a fuel is burnt ?**

**Ans.** When a fuel is burnt, chemical energy is converted into heat and light.

**Q. 11. Why is net calorific value (NCV) less than gross calorific value (GCV) ?**

**Ans.** Gross calorific value is the total amount of heat liberated when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled to room temperature.

Net calorific value is the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape.

As the combustion products are not condensed in net calorific value calculations so lesser amount of heat is available. The net calorific value is less than gross calorific value by the amount of latent heat of steam formed during the complete combustion of one unit of the fuel.

**Q. 12. Define a chemical fuel.**

**Ans.** A chemical Fuel can be defined as any combustible substance containing carbon as the main constituent which during combustion gives large amount of industrially and/or domestically useful heat.

**Q. 13. How are chemical fuels classified ? Give suitable examples for each class.**

[U.P.Tech., March 2002]

**Ans.** Chemical fuels can be classified as follows :

Type of Fuel	Natural or Primary	Artificial or Secondary
Solid	Wood, peat, lignite, Dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum
Gaseous	Natural gas	Coal gas, oil gas, Bio gas, water gas etc.

### Exercises

#### (A) Multiple Choice Questions

- An example of primary fuel is :  
 (a) Lignite (b) Coke (c) Coal gas (d) charcoal.
- The hydrocarbon having 100 octane number is :  
 (a) Iso-heptane (b) n-octane  
 (c) 2, 3-dimethyl pentane (d) 2, 2, 4-trimethyl pentane
- A fuel having high ignition temperature is :  
 (a) Petrol (b) Wood (c) Kerosene (d) LPG
- The calorific value of a fuel is expressed in :  
 (a) kcal cm (b) kcal/cm<sup>3</sup> (c) kcal/m<sup>3</sup> (d) Cal/m<sup>3</sup>

5. Octane number tells the quality of :  
 (a) Petrol (b) Diesel (c) Kerosene oil (d) lubricating oil.
6. Petrol is a mixture mainly of :  
 (a) alkanes (b) alkenes  
 (c) alkynes (d) Aromatic hydrocarbons.
7. Which of the following hydrocarbon isomers have the highest octane rating ?  
 (a)  $\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} \\ | \quad | \\ \text{C} \quad \text{C} \end{array}$  (b)  $\text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C}$   
 (c)  $\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ | \\ \text{C} \end{array}$  (d)  $\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ | \\ \text{C} \end{array}$
8. A good fuel should have :  
 (a) high moisture content (b) low calorific value  
 (c) high ash content (d) moderate ignition temperature.
9. Bergius process of synthetic petrol involves mainly :  
 (a) passing water gas over heated powdered coke under pressure.  
 (b) catalytic hydrogenation of coal (c) heating coal alone under pressure  
 (d) cracking of heavy oil.
10. Main constituent of LPG is :  
 (a) Methane (b) butane (c) propane (d) benzene.
11. Bomb calorimeter is based upon the principle :  
 (a) Action and reaction are equal and opposite.  
 (b) Mass can be neither created nor destroyed.  
 (c) Heat lost by complete combustion of fuel is equal to heat gained by water and calorimeter.  
 (d) None of the above.
12. The quality of the coal is assessed by  
 (a) Proximate and ultimate analysis (b) Gravimetric analysis  
 (c) Volumetric analysis (d) Complexometric analysis.
13. Domestic cooking gas is  
 (a) Mixture of propane and butane  
 (b) Mixture of different hydrocarbons  
 (c) Mixture of methane and ethane  
 (d) Mixture of methane and benzene.
14. The quality of gasoline depends upon :  
 (a) Octane number (b) Gold number (c) Cetane number (d) Steam number
15. Name of domestic gaseous fuel used is  
 (a) Oil gas (b) Coal gas  
 (c) Liquid petroleum gas (d) Producer gas
16. Biogas is produced by  
 (a) Degradation of biological matter by anaerobic bacteria action  
 (b) Cracking of kerosene  
 (c) Destructive distillation of coal  
 (d) The action of steam on coke at high temperature.



17. The quality of diesel fuel depends on :  
 (a) octane number (b) gold number  
 (c) steam number (d) cetane number.
18. The correct relation between GCV and NCV is  
 (a)  $GCV > NCV$  (b)  $GCV = NCV$   
 (c)  $GCV < NCV$  (d)  $GCV = NCV + 0.09 H \times 587$
19. The main combustible constituent present in coal is  
 (a) H (b) C (c) N (d) S
20. Which is the natural fuel ?  
 (a) Coal (b) Coke (c) Petrol (d) diesel

**Answers**

- |         |         |         |         |
|---------|---------|---------|---------|
| 1. (a)  | 2. (d)  | 3. (b)  | 4. (c)  |
| 5. (a)  | 6. (a)  | 7. (a)  | 8. (d)  |
| 9. (b)  | 10. (b) | 23. (a) | 14. (a) |
| 11. (c) | 12. (a) | 17. (d) | 18. (d) |
| 15. (b) | 16. (a) |         |         |
| 19. (b) | 20. (a) |         |         |

**(B) Fill in the Blanks**

- \_\_\_\_\_ are materials that can be utilized to generate energy.
- \_\_\_\_\_ are substances, whose exothermic reaction with oxygen during combustion could be used as a source of heat and power.
- The term \_\_\_\_\_ is used for coal and crude petroleum which were formed from the fossilized remains of plants and animals.
- The \_\_\_\_\_ is an empirical but important analysis which records moisture, volatile matter, ash and fixed carbon as percentages of the original weight of the coal sample.
- The \_\_\_\_\_ is the determination of the ultimate constituents in dry coal and reports constituents such as C, H, O, N, S, P, Cl, As, V, etc.
- Proximate analysis, together with \_\_\_\_\_ (a) and \_\_\_\_\_ (b), furnishes most of the important data necessary to assess the usefulness of a given sample of coal and to grade coals of the same rank.
- Fuels that burn with a flame have a lower \_\_\_\_\_.
- The decomposition of coal by heating it out of contact with air (destructive distillation) to give a solid residue, coke, is called \_\_\_\_\_.
- The calorific value of coke is generally \_\_\_\_\_ than coal from which it is obtained.
- During petroleum cracking, the products obtained have \_\_\_\_\_ boiling points than the original oil.
- Higher the octane rating of a gasoline \_\_\_\_\_ is its tendency for knocking.
- LPG has \_\_\_\_\_ ignition temperature than that of kerosene.
- The SI unit for expressing the calorific value of a solid fuel is \_\_\_\_\_.
- The process of separation of various fractions of petroleum is known as \_\_\_\_\_.
- The substance with octane number 100 is \_\_\_\_\_.
- \_\_\_\_\_ is the only primary liquid fuel in nature.
- \_\_\_\_\_ calorific value includes latent heat of steam.

18. Alcohol-petrol blend possess better \_\_\_\_\_ properties.
19. Alkaline pyrogallol in Orsat's apparatus is used to absorb \_\_\_\_\_ gas.
20. Cetane number refers to a liquid fuel, used in \_\_\_\_\_.
21. Fuel used in railway locomotive is \_\_\_\_\_.
22. Percentage of fixed carbon can be determined by \_\_\_\_\_.
23. Producer gas is a mixture of \_\_\_\_\_.
24. Water gas is a mixture of \_\_\_\_\_.
25. The minimum temperature at which an oil gives off sufficient vapours to form a combustible mixture with air is known as \_\_\_\_\_.
26. Combustion of fuel involves chemical reaction between fuel and \_\_\_\_\_.
27. In combustion of fuels \_\_\_\_\_ reaction occurs.
28. The unit of calorific value of solid fuel is \_\_\_\_\_.
29. Nitrogen in a fuel can be determined by \_\_\_\_\_.
30. The GCV and NCV of solid fuel can be determined by using \_\_\_\_\_ calorimeter.

### Answers

- |   |                           |
|---|---------------------------|
| 1. Fuel                                     | 2. Chemical fuels         |
| 3. Fossil fuel                              | 4. Proximate analysis     |
| 5. Ultimate analysis                        |                           |
| 6. (a) Calorific value, (b) Sulphur content | 7. Calorific intensity    |
| 8. Carbonization                            | 9. Higher                 |
| 10. Lower                                   | 11. Lesser                |
| 12. Lower                                   | 13. kJ/kg                 |
| 14. fractional distillation                 | 15. Isooctane             |
| 16. Petroleum                               | 17. Gross or Higher       |
| 18. Antiknock                               | 19. Oxygen                |
| 20. Diesel engines                          |                           |
| 21. diesel                                  | 22. proximate analysis    |
| 24. CO and H <sub>2</sub> O                 | 23. CO and N <sub>2</sub> |
| 25. ignition temperature                    | 26. oxygen                |
| 27. exothermic                              | 28. Cal/g or J/g          |
| 29. ultimate analysis                       |                           |
| 30. bomb's                                  |                           |

(C) Match the following :

**A**  
(Catalyst in Fisher-Tropsch  
Synthesis)

- (i) Co or Fe catalyst
- (ii) ZnO - Cr<sub>2</sub>O<sub>3</sub>
- (iii) ThO<sub>2</sub> or ZnO - Al<sub>2</sub>O<sub>3</sub>
- (iv) Ru
- (v) Anthracite
- (vi) Antiknocking agent

**B**  
(Main  
Products)

- (a) Higher hydrocarbons
- (b) Hydrocarbons
- (c) Methanol and other alcohols
- (d) A mixture of saturated and unsaturated hydrocarbons
- (e) Tetra ethyl lead
- (f) Highest calorific value

(vii) Reforming	(g) Ethanol blended gasoline
(viii) Synthetic petrol	(h) Removal of olefins and sulphur compounds
(ix) Refining	(i) Petrol from non-petroleum source
(x) Power alcohol	(j) Structural modification of gasoline
(xi) Petrochemicals	(k) Presence of oxygen
(xii) Naphtha	(l) Burning wastes in large furnaces
(xiii) Carbonisation	(m) Aerobic method of decomposition
(xiv) Bomb calorimeter	(n) Volatile liquids
(xv) Gasoline	(o) Moisture content
(xvi) Boy's calorimeter	(p) Non-volatile liquids
(xvii) Proximate Analysis	(q) C <sub>5</sub> - C <sub>9</sub>
(xviii) Composting	(r) Absence of oxygen
(xix) Incineration	(s) C <sub>9</sub> - C <sub>10</sub>
(xx) Combustion	(t) Derived from crude oil and natural gas

**Answer**

1. (i) - (d) ; (ii) - (c) ; (iii) - (b) ; (iv) - (a) ; (v) - (f) ; (vi) - (e) ; (vii) - (j) ; (viii) - (i) ;  
 (ix) - (h) ; (x) - (g) ; (xi) - (t) ; (xii) - (s) ; (xiii) - (r) ; (xiv) - (p) ; (xv) - (q) ; (xvi) - (n) ;  
 (xvii) - (o) ; (xviii) - (m) ; (xix) - (l) ; (xx) - (k)

**(D) State True and False**

- The process of splitting bigger hydrocarbons into smaller hydrocarbons is called cracking.
- Ignition temperature of solid fuel is high.
- Combustion is a chemical reaction of fuel with oxygen resulting in the production of heat, light and flame.
- Synthetic and secondary fuels are one and the same thing.
- Moisture, volatile matter, ash and fixed carbon present in coal can be determined by proximate analysis.
- A good fuel has high calorific value, and low moisture content.
- A good fuel must be most suitable for a given application.
- GCV is always higher than or equal to NCV.
- If a fuel does not have hydrogen as one of its constituents, then GCV = NCV.
- Ultimate analysis can be done to find the %S in given fuel.

**ANSWERS**

- |         |          |         |         |
|---------|----------|---------|---------|
| 1. True | 2. True  | 3. True | 4. True |
| 5. True | 6. True  | 7. True | 8. True |
| 9. True | 10. True |         |         |



**(E) Differentiate between the following :**

1. Fixed bed catalytic cracking and fluidised bed catalytic cracking.
2. Synthetic petrol and power alcohol.
3. Proximate analysis and ultimate analysis.
4. Caking coal and coking coal.
5. Octane number and cetane number.
6. Thermal cracking and catalytic cracking.
7. High and low temperature carbonization.

**(F) Short Answer Type Questions**

1. What is meant by calorific intensity of coal ?
2. Why should an ideal fuel have moderate ignition temperature ?
3. Why is the oxidation of fuel a self sustaining process?
4. Why a good fuel must have low ash content ?
5. Why are no aromatic compounds found in gases or gasoline fractions ?
6. What is the importance of the determination of fixed carbon in coal ?
7. What is wet gas ?
8. Why is it necessary to remove sulphur compounds from oil and natural gas ?
9. Why does coal evolve more heat on burning ?
10. What is meant by sweetening of petrol ?
11. What is meant by compression ratio of an I.C. engine ?
12. What are petrochemicals ?
13. What are fossil fuels and how are they formed ?
14. What are flue gases ?

**Numerical Problems****Type A : (Based on the Combustion of Fuel)**

1. A gas has the following composition by volume :  $H_2 = 20\%$  ;  $CH_4 = 6\%$  ;  $CO = 22\%$  ;  $CO_2 = 4\%$  ;  $O_2 = 4\%$  and  $N_2 = 44\%$ . 20% excess air is used. Find the weight of air actually supplied per  $m^3$  of this gas. Mol. Wt. of air = 28.97. (Ans. 2143 g)
2. A gaseous fuel has the following composition by volume :  $H_2 = 22\%$  ;  $CH_4 = 4\%$  ;  $CO = 22\%$  ;  $CO_4 = 6\%$  ;  $N_2 = 45\%$ . If 20% excess of air is used, find the weight of air actually supplied per  $m^3$  of the gas. (Ans. 2215 g)
3. Calculate the volume of air (volume % of oxygen in air = 21) required for the complete combustion of one litre of CO. (Ans. 2.381 L)
4. A producer gas has the following composition by volume :  $CH_4 = 3.5\%$  ;  $CO = 25\%$  ;  $H_2 = 10\%$  ;  $CO_2 = 10.8\%$  ;  $N_2 = 50.7\%$ . Calculate the theoretical quantity of air required per cubic meter of the gas. (Ans.  $1.167 m^3$ )
5. Calculate the mass and volume of air needed for the combustion of 1 kg of carbon. (Ans. 11.596 kg ;  $8.975 m^3$  at STP)

6. A furnace oil contains 80% carbon and 20% hydrogen by weight. Determine the weight of air required per kg of oil, if 20% excess air is used for complete combustion of oil. (Ans. 19.48 kg)
7. Calculate the weight of air needed for complete combustion of 5.0 kg of a coal containing 80% carbon, 15% hydrogen and the rest oxygen. (Ans. 71.39 kg)
8. A sample of fuel contains the following by weight : carbon = 81% ; hydrogen = 4% ; oxygen = 2% ; nitrogen = 10% ; sulphur = 1%, remainder ash. Calculate the volume of air required for the perfect combustion of 1 kg of fuel, assuming STP conditions. (Ans. 8.319 m<sup>3</sup> at STP)
9. A sample of coal was found to have the following percentage composition : C = 75% ; H = 5.2% ; O = 12.8% ; S = 1.2% ; N = 3.7% ; ash = 2.1%. Calculate the minimum amount of air necessary for complete combustion of 1 kg of coal. (Ans. 10 kg)

### Type B : (Based on Calorific Value Determination)

1. When 0.935 g of a fuel underwent complete combustion in excess of oxygen, the increase of temperature of water in a calorimeter containing 1365 g of water was 2.40°C. Calculate the higher calorific value of the fuel, if the water equivalent of calorimeter, etc., is 135 g. (Ans. HCV = 3850.3 cal/gm)
2. Liquid fuel weighing 0.98 g and containing 90% of carbon and 8% of hydrogen gave the following results in a bomb calorimeter experiment : Amount of water taken in the calorimeter = 1450 g ; water equivalent of the calorimeter = 450 g ; rise in temperature of water = 1.8°C. If the latent heat of steam is 587 cal/g, calculate the gross and net calorific value of the fuel. (Ans. GCV = 3,490 cal/g ; NCV = 3,067 cal/g)
3. The temperature of 950.0 g of water increased from 5°C to 28.5°C on burning 0.75 g of a solid fuel in a bomb calorimeter. Water equivalent of calorimeter and latent heat of steam are 400.0 g and 587.0 cal/g respectively. If the fuel contains 0.65% of hydrogen, calculate its net calorific value. (Ans. 5,366 cal/g)
4. A sample of coal containing 92% C ; 5% H ; 3% ash. When this coal was tested in the laboratory for its calorific value in the bomb calorimeter, the following data were obtained :

Weight of Coal Burnt	= 0.95 g
Weight of Water Taken	= 700 g
Water equivalent of bomb and calorimeter	= 2000 g
Rise in temperature	= 2.48°C
Cooling correction	= 0.02°C
Fuse wire correction	= 10.0 cal
Acid correction	= 60.0 cal

Calculate the net and gross calorific values of the coal in cal/g ; (Assume the latent heat of condensation of steam as 580 cal/g).

(Ans. GCV = 7031.6 cal/g ; LCV = 6770.6 cal/g)

5. The determination of the calorific value of a coal sample gave the following data :

Wt. of coal sample	= 0.9 g
Water equivalent of calorimeter	= 440 g
Wt. of water	= 2500 g
Rise in temperature	= 2.42°C
Cooling correction	= 0.052°C
Fuse-wire correction	= 10.0 calories.



Calculate the gross and net calorific values, if the coal contains 6% hydrogen and assume latent heat of steam equal to 600 cal/g.

(Ans. (i) 8064.1 cal/g ; (ii) 7740.1 cal/g)

6. 0.834 g of a fuel on complete combustion in excess of oxygen increased the temperature of water in a calorimeter from 14.36°C to 18.10°C. The mass of water in calorimeter was found to be 1365 g. Calculate the higher calorific value of the fuel, if the water equivalent of calorimeter, etc., is 135 g.

(Ans. 6726.6 cal/g)

7. The following data were obtained in a Boys' gas calorimeter experiments :

Volume of gas used = 0.1 m<sup>3</sup> at STP

Wt. of water heated = 25 kg

Temperature of inlet water = 20°C

Temperature of outlet water = 33°C

Wt. of steam condensed = 0.025 kg.

Calculate the higher and lower calorific value per m<sup>3</sup> at STP. Take the heat liberated in condensing water vapour and cooling the condensate at 580 kcal/kg.

(Ans. HCV = 3250 kcal/m<sup>3</sup> ; LCV = 3105 kcal/m<sup>3</sup>)

8. Calculate the gross and net calorific value of coal sample having the following composition : C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4%.

(Ans. GCV = 8828 kcal/kg ; NCV = 8458 kcal/kg)

9. A sample of coal was found to have the following percentage composition :

C = 75% ; H = 5.2% ; O = 12.1% ; N = 3.2% and ash = 4.5%

- (i) Calculate the minimum amount of air necessary for complete combustion of 1 kg of coal.

- (ii) Also calculate the HCV and LCV of the coal sample.

(given : gross C.V. of carbon = 8080 kcal/kg, hydrogen = 34500 kcal/kg and sulphur = 2240 kcal/kg)

(Ans. (i) 9.978 kg (ii) 7332 kcal/kg ; 7057 kcal/kg)

### Type C : (Based on Proximate and Ultimate analysis)

1. A sample of coal was analysed as follows : 1.000 g of an air-dried coal, sample was weighed in a silica crucible. After heating for 1 hour at 105 – 110°C, the dry coal residue weighed 0.985 g. The crucible was covered with a vented lid and then heated strongly for exactly 7 minutes at 950 ± 20°C. The residue weighed 0.800 g. The crucible was then heated strongly in air, until a constant weight was obtained. The last residue was found to weigh 0.100 g. Calculate the proximate analysis.

(Ans. Moisture = 1.5% ; volatile matter = 18.5% ; ash = 10.0% ; and fixed C = 70.0%)

2. A sample of the Gondwana coal of Jharia was analysed as follows : Exactly 2.500 g was weighed into a silica crucible. After heating for 1 hour at 110°C, the residue weighed 2.415 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes at 950 ± 20°C. The residue weighed 1.528 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.245 g. (i) Calculate the percentage results of the above analysis. (ii) To which type of analysis does the above description belong ? Why is the analysis so-named ?

(Ans. Moisture = 3.4% ; volatile matter = 35.48% ; ash = 9.80% ; and fixed C = 51.32%)



3. 1.56 g of the coal was kjeldahlized and  $\text{NH}_3$  gas thus evolved was absorbed in 50.0 mL of 0.1 N  $\text{H}_2\text{SO}_4$ . After absorption, the excess (residual) acid required 6.25 mL of 0.1 N NaOH for exact neutralization. 2.60 g of the coal sample in a quantitative analysis gave 0.1755 g of  $\text{BaSO}_4$ . Calculate the percentage of N and S in the coal sample.  
(Ans. N = 3.926% ; S = 0.927%)
4. 0.5 g of a sample of coal was used in a bomb calorimeter for the determination of calorific value. Calorific value of coal was found to be 8600 cal/g. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with barium nitrate solution and a precipitate of barium sulphate was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.05 g. Calculate the percentage of sulphur in the coal sample. (Ans. 1.3734%)
5. 1.0 g of a sample of coal was used for nitrogen estimation by kjeldahl method. The evolved ammonia was collected in 25 mL (N/10) sulphuric acid. To neutralise excess acid, 15 mL of 0.1 N sodium hydroxide was required. Determine the percentage of nitrogen in the given sample of coal. (Ans. 1.4%)

#### Type D : (Based on Flue Gas Analysis)

1. A coal sample gave the following analysis : C = 66.2% ; H = 4.2% ; O = 6.1% ; N = 1.4% ; S = 2.9% ; moisture = 9.7% and ash = 9.5%. Determine the quantity of products of combustion, if 1 kg of coal is burnt with 25% excess air.  
(Ans. 12.1763 kg)
2. The percentage composition of a sample of bituminous coal was found to be as under : C = 75.4, H = 5.3, O = 12.6, N = 3.2, S = 1.3, the rest being ash. Calculate the minimum weight of air necessary for complete combustion of 1 kg of coal and percentage composition of the dry products of combustion by weight.  
(Ans.  $\text{CO}_2$  = 26.172% ;  $\text{SO}_2$  = 0.246% ;  $\text{N}_2$  = 73.58%)
3. The coal has the following analysis : C = 54.0% ; H = 6.5% ; O = 3.0% ; N = 1.8% ; moisture = 17.3%, and remaining is ash. This coal on combustion with excess of air, gave 21.5 kg of dry flue gases per kg of coal burnt. Calculate the percentage of excess air used for combustion. (Ans. 155.3 %)
4. The composition of a producer gas was found to be :  $\text{H}_2$  = 14% ;  $\text{CH}_4$  = 2% ; CO = 22% ;  $\text{CO}_2$  = 5% ;  $\text{N}_2$  = 55% and  $\text{O}_2$  = 2% by volume. Find the air required for the perfect combustion of 1  $\text{m}^3$  of this gas. If 40% excess air is used. Find the volume analysis of the dry products of combustion.  
(Ans. (i) 0.952  $\text{m}^3$  ; (ii)  $\text{CO}_2$  = 14.70%,  $\text{O}_2$  = 4.05%, and  $\text{N}_2$  = 81.25%)
5. The percentage composition of a sample of coal by weight was found to be : C = 76% ; H = 5.2% ; O = 12.8% ; N = 2.7% ; S = 1.2%, the remaining being ash. Calculate the minimum : (a) weight, and (b) volume at NTP of air necessary for complete combustion of 1 kg of coal and percentage composition by weight of dry products, if 50% excess air is supplied.  
(Ans. (i) 10.116 kg ; (ii) 7.83  $\text{m}^3$  ;  $\text{N}_2$  = 74.7%,  $\text{O}_2$  = 7.417% and  $\text{SO}_2$  = 0.153%,  $\text{CO}_2$  = 17.77%)
6. An oil on analysis, gave the following results by weight : C = 86% ; H = 11.75% and O = 2.25%. Find the weight of minimum air required for burning 1 kg of the fuel, also obtain the products.  
(Ans. (a) 13.960 kg ; (b)  $\text{CO}_2$  = 3.153 kg ;  $\text{H}_2\text{O}$  = 1.058 kg ;  $\text{N}_2$  = 10.749 kg)

7. A sample of coal was found to contain the following : C = 81% ; H = 4% ; O = 2% ; N = 10%, the remaining being ash.  
Estimate the quantity of minimum air required for complete combustion of 1 kg of the sample. Find the composition of dry fine gas by volume, if 40% excess air is supplied.  
(Ans. (i) 10.697 kg ; (ii)  $\text{CO}_2 = 13.23\%$  ;  $\text{N}_2 = 80.74\%$ , and  $\text{O}_2 = 6.029\%$ )
8. Calculate the minimum weight and volume (at NTP) of air required for complete combustion of 1 kg of coal having the following percentage composition by weight : C = 90.0, H = 3.5, O = 3.0, S = 0.5, N = 0.5 and ash = 2.5. Also calculate the percentage composition by weight of the dry products of combustion (ash not included).  
(Ans. (i) 11.5435 kg ; (ii)  $8.938 \text{ m}^3$  ;  $\text{CO}_2 = 27.041\%$  ;  $\text{N}_2 = 72.877\%$ )
9. Analysis of coal used in boiler is : C = 82% ; H = 4.2% ; O = 4.8% ; ash = rest. When this coal was used in a boiler, the analysis of flue gas was :  $\text{CO}_2 = 10\%$  ; CO = 1.5% ;  $\text{O}_2 = 8.0\%$  ;  $\text{N}_2 = 80.5\%$ . Determine (i) the amount of excess air per kg of coal burnt, (ii) total mass of air supplied per kg of coal burnt, (iii) percentage of excess air supplied for combustion.  
(Ans. (i) 5.970 kg (ii) 16.731 kg (iii) 55.5 %)
10. A fuel has the following percentage composition by mass :  $\text{H}_2 = 24.0$ ,  $\text{CH}_4 = 35.0$ ,  $\text{C}_2\text{H}_6 = 6.0$ ,  $\text{CH}_2\text{H}_4 = 5.0$ ,  $\text{C}_4\text{H}_2 = 2.5$ , CO = 7.6,  $\text{CO}_2 = 6.5$ ,  $\text{O}_2 = 0.6$  and  $\text{N}_2 = \text{rest}$ . Calculate the minimum amount of air required at  $25^\circ\text{C}$  and 1 atm pressure for complete combustion per kg of fuel burnt. Also give the volumetric analysis of flue gas obtained.  
(Ans. Minimum. weight of air required for 1 kg of fuel burnt = 16.69 kg  
Volume of air at STP = 12.918 L Volume of air at  $25^\circ\text{C}$  and 1 atm =  $14.101 \text{ m}^3$   $\text{CO}_2 = 7.10\%$  and  $\text{N}_2 = 92.9\%$ )

## Lubricants

Anybody can become angry – that is easy ; But to be angry with the right person, and to the right degree, and at the right time, and for the right purpose, and in the right way – that is not within everybody's power and is not easy.

### 1 INTRODUCTION

In all types of machines, the surfaces of moving, sliding or rolling parts rub against each other. This mutual rubbing of one part against another generates *frictional force* which offers resistance to the relative motion of these surfaces. *Wear* results when this resistance is overcome by applied forces. Hence, friction causes a lot of wear and tear of surfaces of moving/sliding/rolling parts which consequently require repeated *replacement*. Friction also generates heat which gets dissipated thereby causing loss in the *efficiency* of the machine.

These drawbacks of frictional resistance can be minimized by applying a thin layer of certain substances, known as *lubricant* in between the moving/sliding/rolling surfaces. A lubricant may thus be defined as a substance which reduces the friction when introduced between two surfaces and the phenomenon is known as *lubrication*.

### 2. FUNCTIONS OF LUBRICANTS

(i) *The first and foremost function of a lubricant is to reduce friction.* Let us consider two steel blocks one on top of the other. Both the steel blocks have smooth

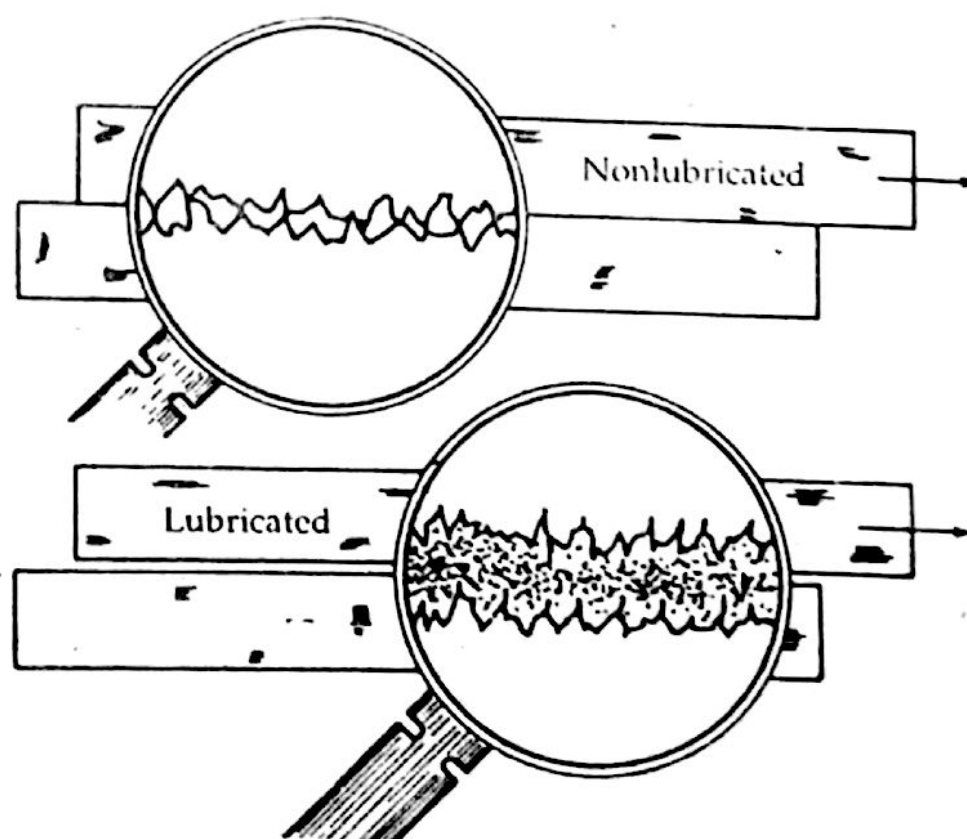


Fig. 1. Lubricants reduce friction.



ground surfaces. Top block can be made to slide over the bottom block by applying force. It is experimentally found that less force is required for this sliding motion when the two steel surfaces are separated by some lubricating oil.

This can be explained by careful analysis of steel surfaces under powerful microscope. This study reveals that steel surfaces actually exhibit minute *peaks* and *valleys* that interlock to prevent the blocks from sliding freely. These peaks are known as *asperities*. The force required to overcome the resistance created by the interlocking asperities and to slide one block past the other is known as the *Frictional Force*. As is shown in Fig. 1, when the two steel surfaces are separated by some lubricating oil, the small peaks and valley do not interlock, and the top block slides very freely over the bottom block.

(ii) *It reduces wear, tear and surface deformation* because the direct contact between the sliding/moving surfaces is avoided. Without the intervening lubricant, some of the small peaks would be sheared off as one block moved over the other. Eventually, this would result in wear, tear and surface deformation.

In actual machinery, excessive wear on any part may result in malfunction of the entire unit. Bearing wear can induce gear misalignment, and in the mill itself, may affect product shape and quality. On an extreme case it may result in breakages, heavy damage and costly delays.

(iii) *It acts as coolant to carry away heat*. In a machine, frictional heat is always produced at the point of contact between the rubbing parts. Cool oil flowing over the heated surface absorbs and carries the heat away. In high speed, high-load sleeve bearings like those used in backup roll serve in hot and cold strip, sheet and tin mills, the heat generated within the oil film is very high because the oil films are very thin and shear rates are high, but as shown in Fig. 2, cool oil flowing through the unloaded side of the bearing meets the heated oil and returns it to the reservoir at a much lower temperature.

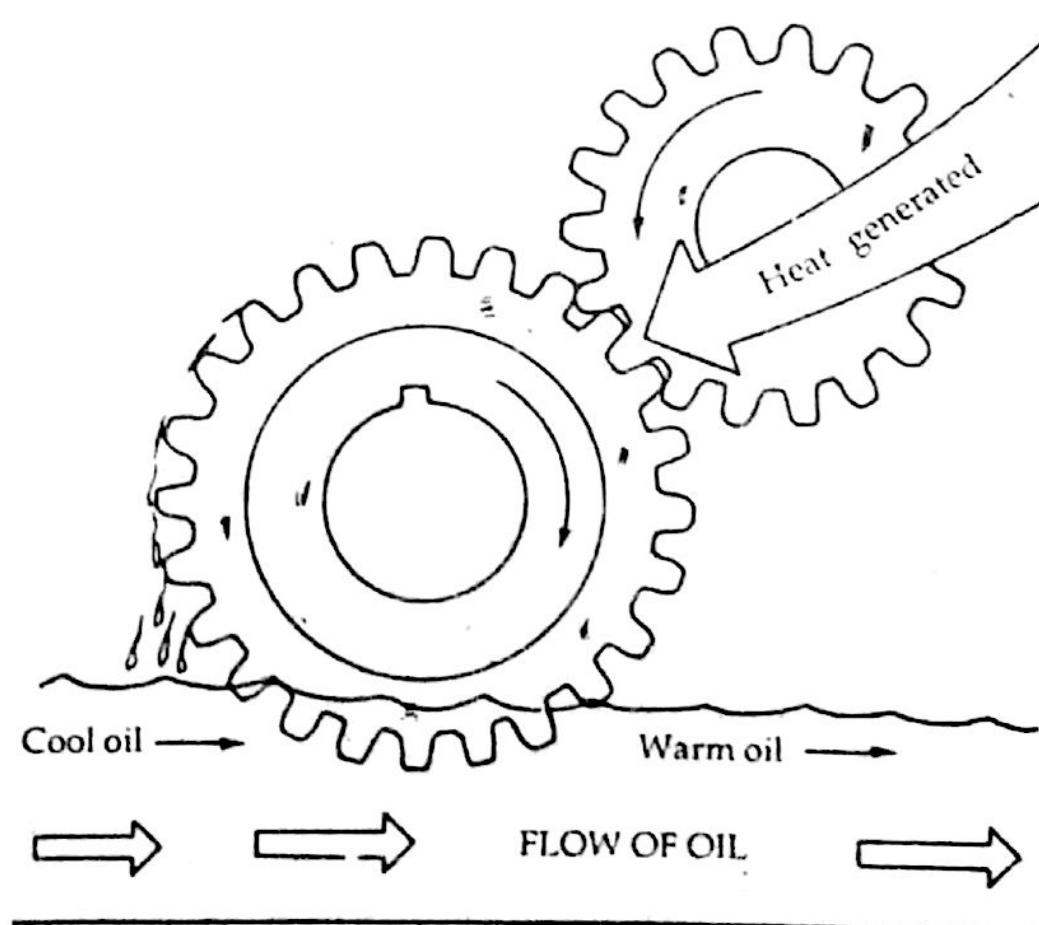


Fig. 2. Lubricants carry away heat.

(iv) *It keeps out dirt.* The proper use of a lubricant can prevent foreign matter or dirt from entering a bearing and damaging the smooth surface of the journal and bearing.

(v) Sometimes, it *acts as a seal*. For example, in an internal combustion engine, the lubricant used between the piston and the cylinder wall acts as a seal. This seal prevents the leakage of gases under high pressure from the cylinder.

(vi) It reduces the maintenance and running cost of the machine as it *prevents rust and corrosion*. Generally, lubricant formulations containing rust inhibitors provide a protective residual film to ward off the attack of an external corrosive substance.

(vii) It *transmits fluid power*. The hydraulic lift that raises automobiles in a service station uses a plunger or piston inside a cylinder for transmitting power or force by means of petroleum oil. The petroleum oil also protects the sliding, contacting surfaces. The viscosity of petroleum oils for this function is low. Moreover they require to be anti wear, rust and oxidation inhibited.

(viii) As the use of lubricant minimizes the liberation of frictional heat hence it avoids seizure of moving surfaces and expansion of metal. It also reduces loss of energy in the form of heat. Hence, it improves the efficiency of the machine.

### 3 MECHANISM OF LUBRICATION

Lubrication mechanism can be classified into following types :

(a) *Hydrodynamic Lubrication or Fluid Film Lubrication.* In this, the moving/sliding surfaces are separated from each other by a bulk lubricant film (at least  $1000 \text{ \AA}$  thick). This bulk lubricant film prevents direct surface-to-surface contact so that the small peaks and valleys do not interlock. This consequently reduces friction and prevents wear. Fluid film lubrication is shown in Fig. 3(a). The small friction (if any) is only due to the internal resistance between the particles of the lubricant moving over each other. In such a system, friction depends on the thickness & viscosity of the lubricant and the relative velocity & area of the moving/sliding surfaces. The coefficient of friction  $= \frac{\text{force required to cause motion (F)}}{\text{Applied load (W)}}$  is as low as 0.001 to 0.03 for fluid film lubricated system in comparison to 0.5 to 1.5 for unlubricated surfaces.

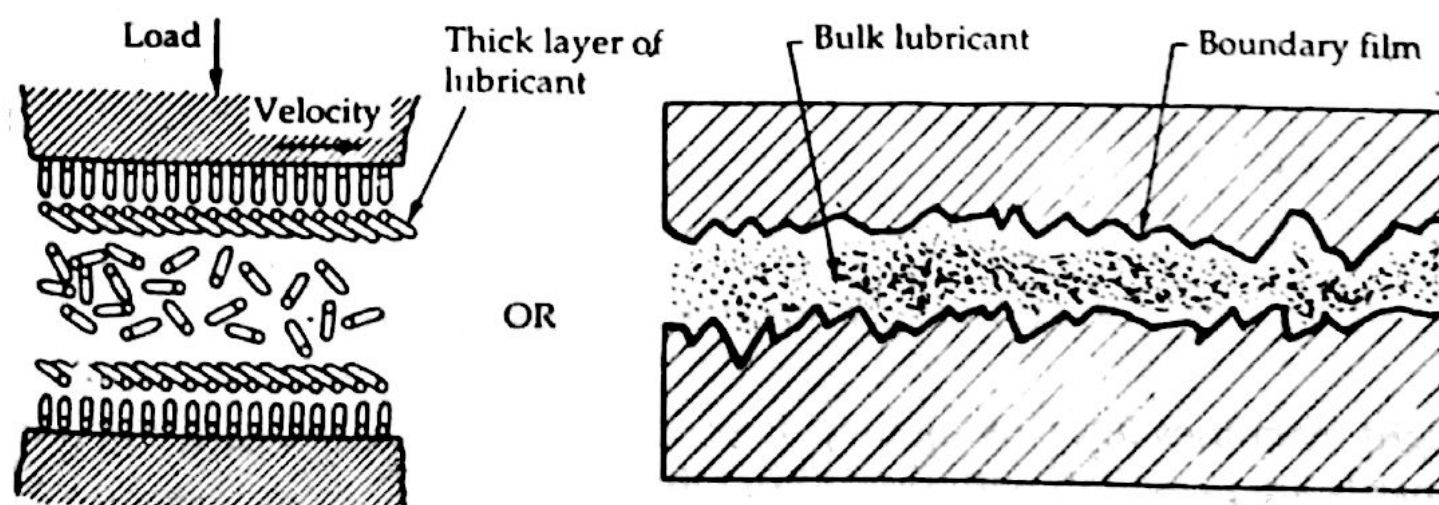


Fig. 3. Fluid film Lubrication – Surfaces separated by Bulk Lubricant film

Let us now consider how the hydrodynamic film is actually generated between a bearing and a rotating journal. Fig. 4(a) shows a journal resting on the bottom of the bearing before motion. Fig. 4(b) shows the oil film which separates the surfaces when the journal rotates. Fig. 5 is a simplified drawing of this process, that shows how, after start up, the journal begins to climb up one side of the bearing; as its pumping action draws oil under it, the journal is forced to the other side by the "oil wedge". At start-up, the coefficient of friction is high in the presence of boundary lubrication. After start-up, however, the coefficient falls rapidly. This is due to the fact that metal surfaces do not come into direct contact with each other. The resistance to movement is only due to the internal resistance of the lubricant.

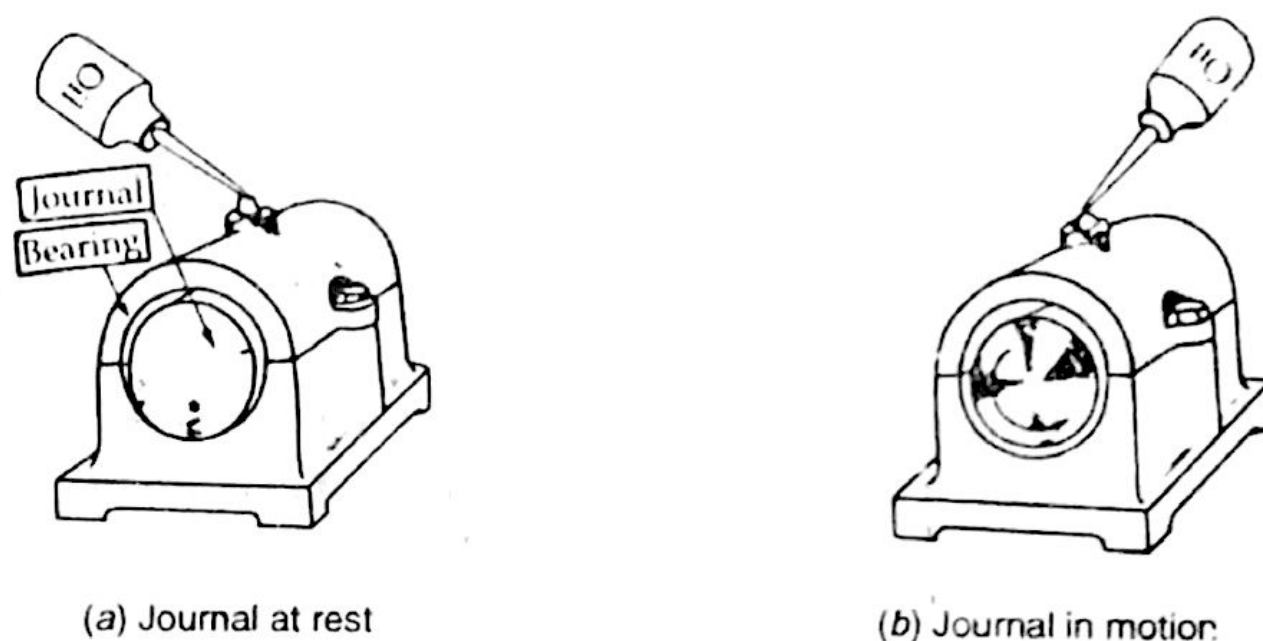


Fig. 4. Formation of oil wedge in a bearing

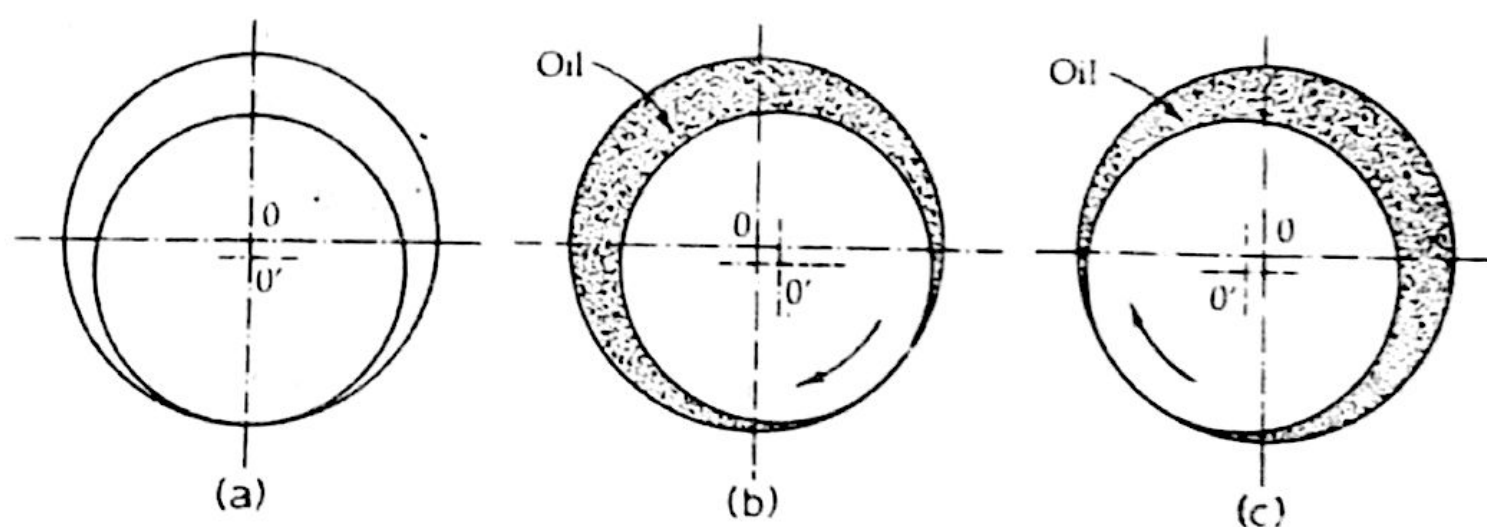


Fig. 5. Formation of fluid film in a plain bearing.

Light machines like sewing machines, watches, clocks, delicate and scientific instruments are provided with fluid-film lubrication.

Fluid film lubrication is satisfactorily done by *hydrocarbon oils*. These are generally blended with selected *long chain polymers* in order to maintain viscosity of the oil constant in all seasons of year.



This is necessary also because the viscosity of hydrocarbon oil decreases with rise in temperature. Hence, an hydrocarbon oil might be satisfactory when an engine is cold but it may become too "thin" to maintain an adequate lubricant film at normal running temperatures.

The viscosity of hydrocarbon oils increases with increasing molecular weight. Hence, for different applications, appropriate fractions from petroleum refining are blended to meet the requirement. But these fractions generally contain small quantity of unsaturated hydrocarbons which get oxidised under operating conditions, forming gums. Hence it is essential that **antioxidants** (like aminophenols) to be blended with hydrocarbon oils.

In practice, some decomposition of these hydrocarbon oils might occur leading to the formation of solid carbon particles. Organometallic 'detergent' compounds need to be added in the oils to keep these carbon particles in suspension in the lubricating oil.

(b) *Boundary Lubrication or thin-film lubrication.* When the lubricant is not viscous enough to generate a film of sufficient thickness to separate the surfaces under heavy loads, friction may yet be reduced with the proper lubricant. Such an application is known as *Boundary lubrication*. Solid lubricants, greases and oils with proper additives function in this manner

A thin layer of lubricant is adsorbed on the metallic surfaces which avoids direct metal-to metal contact. The load is carried by the layer of the adsorbed lubricant on both the metal surfaces (see Fig. 6.) In boundary lubrication, the distance between moving/sliding surface is very small of the order of the height of

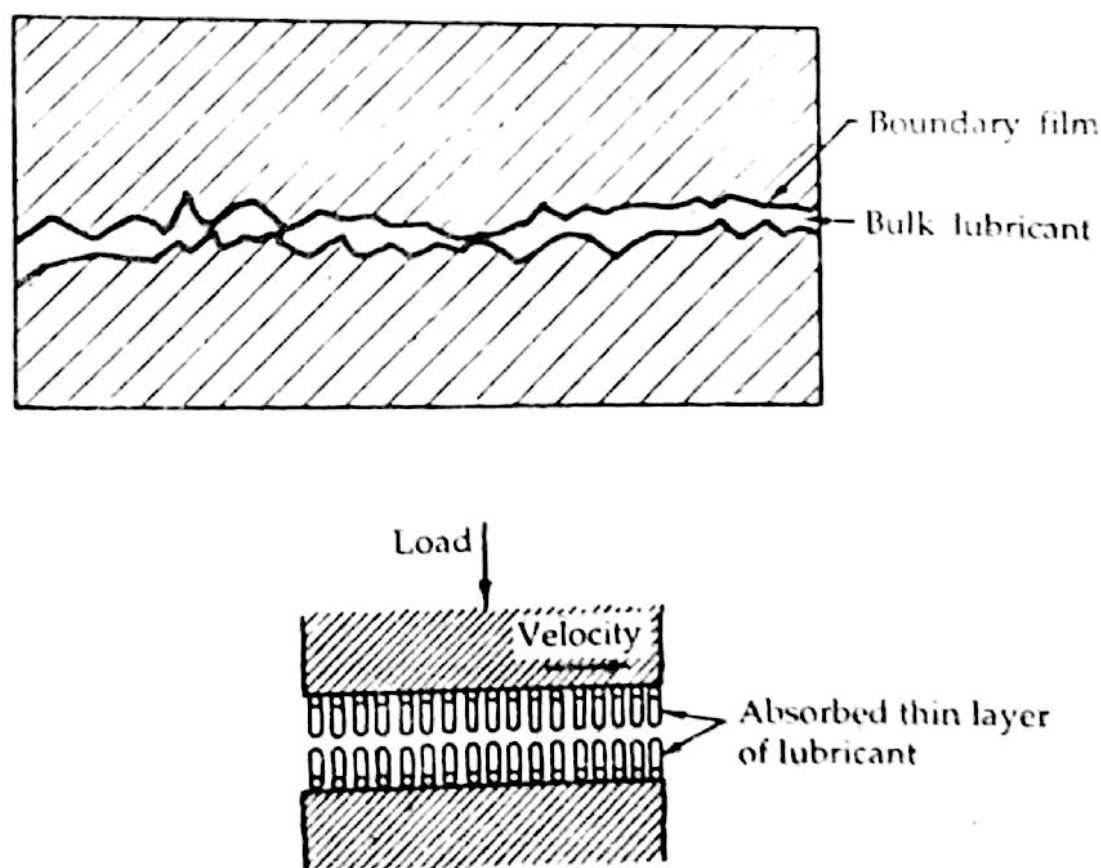


Fig. 6. Boundary lubrication – performance essentially dependent on boundary film.

the surface asperities. The contact between the metal surface is possible by the squeezing out of lubricating oil film. When this occurs the load would be taken on the high spots of the journal and the bearing, and the two surfaces tend to become welded together by the appreciable heat that is generated. This prevents motion as the two surfaces adhere together. This is known as *seizure*. If motion proceeds with the removal of some metal from one of the surfaces the result is known as *scuffing*.

In practice, seizure or scuffing are delayed by the fact that metals tend to form films on their surfaces by chemical action leading to adsorption which temporarily prevents metal to metal contact.

**For boundary lubrication the lubricant molecules should have**

- (i) Long hydrocarbon chains,
- (ii) Lateral attraction between the chains,
- (iii) Polar groups to promote wetting or spreading over the surface,
- (iv) Active functional groups which can form chemical bonds with the metals or other surfaces,
- (v) High viscosity-index ;
- (vi) Resistance to heat and oxidation ;
- (vii) Good oiliness and
- (viii) Low pour and oxidation.

**Lubricants used for boundary lubrication are :**

(i) *Graphite and  $\text{MoS}_2$*  either as solid or as stable emulsion, in oil. These materials reduce friction between metallic surfaces by forming films on the surfaces and they can bear compression as well as high temperature.

(ii) *Mineral oils*. These are thermally stable and their adhesion property (Oiliness is improved by adding small amount of fatty acids or fatty oils.

(iii) *Vegetable and animal oils and their soaps*. They possess greater oiliness compared to mineral oils. They either physically adsorbed to metal surfaces or react chemically at the metal surfaces, forming a thin film of metallic soap, which acts as lubricant.

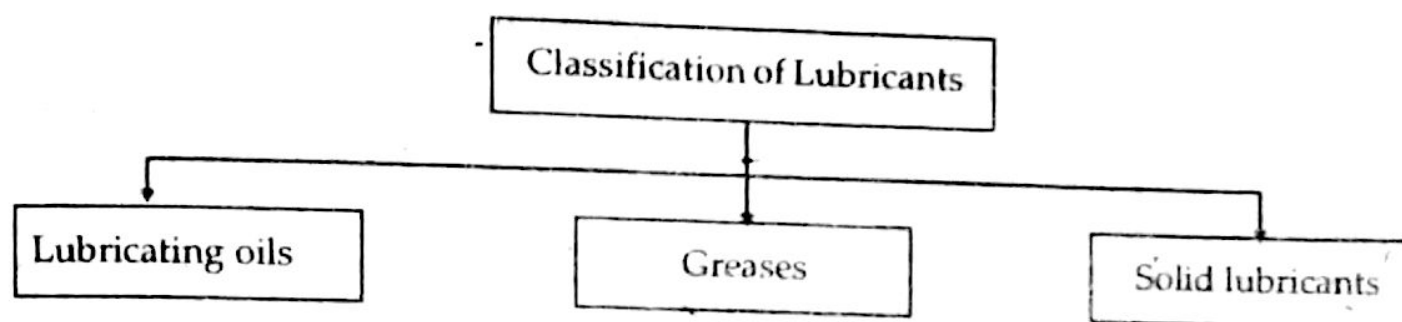
(c) *Extreme-pressure lubrications*. It is done by incorporating extreme pressure additives in mineral oils for applications in which high temperature is attained due to the very high speed of moving/sliding surfaces under high pressure. In such applications, liquid lubricants fail to stick and may decompose and even vaporize.

Chlorinated esters, sulphurized oils and tricresyl phosphate are examples of such additives. These additives react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulphide or phosphides, in the form of durable films. These films can withstand very high loads and high temperatures (because of their high melting points).

Hence, they serve as good lubricant under extreme-pressure and extreme-temperature conditions. These lubricants have an additional advantage that if the low shear strength films formed on the moving parts are broken by the rubbing action, they are immediately replenished.

**Applications which demand lubrication by Extreme pressure additives**

- (i) Wire drawing of titanium (requires chlorine containing additive which reacts with the stable oxide film on the metal surface).
- (ii) In cutting fluids in machining of tough metals. A typical lubricant consists of hydrocarbon oil, a small amount of fatty acid as a boundary lubricant and an organic chloride or sulfide additive.
- (iii) For hypoid gears used in rear axle drive of cars which has both longitudinal sliding motion and normal rolling movement.

**4 CLASSIFICATION OF LUBRICANTS**

On the basis of their physical state, lubricants can be classified as :

- (i) Lubricating oils (or liquid lubricants) ;
- (ii) Greases (or Semi-solid lubricants) ; and
- (iii) Solid lubricants.

**4.1 Lubricating Oils**

Lubricating oils are also known as liquid lubricants and are further *classified* into three categories *viz.* Animal and Vegetable oils, Mineral or Petroleum oils and Blended oils.

**Characteristics of good lubricating oils.** High boiling point, low freezing point, adequate viscosity for proper functioning in service, high resistance to oxidation and heat, non-corrosive properties, and stability to decomposition at the operating temperatures.

**Functions of lubricating oils.** Lubricating oils provide a continuous fluid film in-between moving/sliding/rolling surfaces and reduce friction, wear and heat generation. They also act as cooling and sealing agent. They also prevent corrosion.

The types of lubricating oils are briefly described below :

(a) **Animal and Vegetable oils.** *Animal oils* are extracted from the crude fat by 'rendering' process in which the enclosing tissue is broken by treatment with steam or the combined action of steam and water. Vegetable oils such as cotton seed oil and castor oil are obtained by crushing the seeds. Before use, both animal and vegetable oils require further treatment. This treatment involves cooling (so that sterarine separates out) ; filtration through animal carbon (for removal of colour and brightening the oil ; Neutralization of free fatty acids by requisite amount of alkali ; coagulation treatment with sulphuric acid which removes suspended impurities by carbonizing and causing them to coagulate and settle out) and *filtration*.



Animal and vegetable oils possess good 'oiliness' and hence they stick to the surface of machine parts, even under high temperatures and heavy loads.

	Lubricating oils	Uses
<b>I Animal oils</b>		
	Lard oil	For lubricating ordinary machine parts.
	Neats foot oil	For lubricating clocks and sewing machines particularly suitable for light machinery.
	Sperm oil	Particularly suitable for light machinery.
<b>II Vegetable oils</b>		
	Castor oil	Very good lubricant for bearing and machinery operating at high speeds and low pressures like racing cars.
	Palm oil	For lubricating delicate instruments such as scientific equipment

Animal and vegetable oils have very *limited uses* at present because they are costly, have less resistance to oxidation and after oxidation form gummy and acidic products. They get thickened on coming in contact with air. When allowed to remain in contact with humidity or moisture they show some tendency to hydrolyze.

Actually these oils are used as blending agent for mineral oils so as to produce, desired effects in the latter.

(b) **Mineral or Petroleum oils.** These are basically lower molecular weight hydrocarbons with about 12 to 50 carbon atoms. Their viscosity increases with the length of the hydrocarbon chain. They are obtained by distillation of petroleum. As they are cheap, available in abundance and stable under service conditions, hence they are widely used. In comparison to animal and vegetable oils, oiliness of mineral oils is less. The addition of higher molecular weight compounds like oleic acid and stearic acid, increases the oiliness of mineral oil.

**Purification.** Impurities like wax, asphalt, etc. must be removed from crude liquid petroleum oils before they are used. A number of processes are used for removing these unwanted impurities.

**Dewaxing** means removal of wax from the oil otherwise the wax raises the pour-point and makes lubricating oil unfit for use at low temperatures. For dewaxing, oil is mixed with propane, trichloro ethylene or any other suitable solvent and then refrigerated for the precipitation of wax. Wax is then removed from oil by passing the oil wax suspension through a centrifuge working at 1700 rpm. Finally, distillation is done for solvent recovery.

**Acid refining** means treatment with conc.  $H_2SO_4$  so that asphaltic and naphthenic impurities and other undesirable constituents can be eliminated from dewaxed-oils. Unwanted impurities either get dissolved in acid or are converted into tarry sludges. Sludge is removed by filtration, while the filtrate is neutralized with a calculated amount of caustic soda for the removal of excess of acid. Finally, the oil is decolorised by passing through fuller's earth.

**Solvent refining** involves mixing oil with nitrobenzene or some other suitable solvent (like dichloro ethyl ether, furfural, mixture of propane and cresol or sulphur

dioxide and benzene, etc). Solvent is such in which oil is immiscible but the undesirable impurities are highly soluble. After proper mixing with such solvent, the oil is left undisturbed for some time so that liquid separates into two layers. 'Solvent layer' containing impurities and 'oil layer' free from impurities, but it might contain some solvent which can be recovered by distillation. Distillation also produces refined oil. Solvent is also recovered by similarly distilling 'solvent layer', when the residue containing asphaltic, naphthenic and resinous substances is left behind and is used as a source of these or as a fuel oil. It is to be noted that asphalt undergo decomposition at higher temperatures, causing carbon decomposition and sludge formation. We can reduce any chance of formation of carbon deposits by removing asphaltic materials through solvent refining. This process of solvent refining is economical also and the refined oil thus obtained shows less change in viscosity with temperature. Natural oxidation inhibitors present in oil also get removed during solvent refining. Hence, solvent refined oil shows less resistant to oxidation. Moreover, it possesses lower oiliness. These drawbacks can be removed by incorporating some additives in solvent refined oils.

(c) **Blended oils.** Desirable characteristics of lubricating oils can be improved by adding small quantities of various additives. The oils thus obtained are known as blended oils or compounded oils.

An *additive* is a material that imparts a new or desired property to the lubricating oil. It may also enhance a desirable property that the lubricating oil already possesses to some degree. Broadly speaking, there are two types of lubricant additives :

*Chemically active additives* are those which chemically interact with metals (to form protective films) and with polar oxidation and degradation products (to make them harmless). Dispersants, Detergents Anti-Wear (AW) agents, Extreme Pressure (EP) agents, Oxidation inhibitors, Rust and corrosion inhibitor are few of the examples of chemically active additives.

*Chemically inert additives* are those additives which improve the physical properties that are critical to the effective performance of the lubricant. These additives include : viscosity index improvers, foam inhibitors, Pour point depressants, Demulsifiers, Emulsifiers etc.

These additives, their purpose, functions and typical examples are summarized below :

**(I) Lubricant Protective Additives : -**

<i>Additive Type</i>	<i>Purpose</i>	<i>Functions</i>	<i>Typical examples</i>
(i) Antioxidant	Retard oxidative decomposition	Terminate free radical chain reactions and Decompose peroxides	Aromatic amines, Hindered phenols etc.
(ii) Metal Deactivator	Decrease catalytic effect of metals on oxidation rate	By complexing with metal ions, they form inactive layer on metal surfaces	Amines, sulfides or phosphites etc.
(iii) Antifoamant	Prevent persistent foam formation by lubricant	Speed collapse of foam by reducing surface tension	Silicon polymers.



**(II) Surface Protective Additives**

<i>Additive Type</i>	<i>Purpose</i>	<i>Functions</i>	<i>Typical examples</i>
Rust and Corrosion inhibitor	Prevent rusting and corrosion of metal parts in contact with the lubricant.	Neutralization of corrosive acids and /or preferential adsorption of polar constituent on metal surface to provide a protective film.	Metal phenolates, basic metal sulfonates, fatty acids and amines.
Anti-wear and EP agent	Reduce friction and wear and prevent scoring and seizure	Prevent metal-to-metal contact by chemical reaction with metal surface to form a film with lower shear strength than the metal	Zinc dithiophosphates, organic phosphates and acid phosphates, sulfurized fats etc.
Friction modifier	Change coefficient of friction	Preferential adsorption of surface active materials.	High molecular wt. organic phosphorus and phosphoric acid esters, organic fatty acids and amines.
Detergent	Keep surfaces deposits free	Neutralize the sludge and varnish precursors and keep them soluble.	Magnesium phenolates, phosphates and sulfonates.
Dispersant	Keep insoluble contaminants dispersed in the lubricant	Prevent agglomeration of contaminants as they are bonded by polar attraction to dispersant molecules. Contaminants are kept in suspension due to solubility of dispersant.	Alkylsuccinimides, and polymeric alkylthiophosphonates.

**III. Performance Additives**

<i>Additive Type</i>	<i>Purpose</i>	<i>Functions</i>	<i>Typical examples</i>
(i) Viscosity modifier	Reduce the rate of viscosity change with temperature	Polymer expand with increasing temperature to counteract oil thinning	Polymers and copolymers of olefins, alkylated styrenes, methacrylates and butadiene.



	<i>Additive Type</i>	<i>Purpose</i>	<i>Functions</i>	<i>Typical examples</i>
(ii)	Pour point depressant	Enable lubricant to flow at low temperatures	Reduce interlocking by modifying wax crystal formation	Polymethacrylates, phenolic polymers and alkylated naphthalene.  Aromatic hydrocarbons and organic phosphates.
(iii)	Seal Swell Agent	Cause swelling of elastomer by chemical reaction		

#### 4.2 Greases or Semi-Solid Lubricants

A semi-solid lubricant obtained by combining lubricating oil with thickening agent is termed as "Grease". Lubricating oil is the principal component and it can be either petroleum oil or a synthetic hydrocarbon of low to high viscosity. The *thickeners* consist primarily of special soaps of lithium, sodium, calcium, barium, aluminium etc. Non-soap thickeners include carbon black, silica gel, polyureas and other synthetic polymers, bentonite clays etc. (They improve the heat resistance of a lubricant). The fibrous structure of the thickener traps the oil and enables the lubricant to cling to moving parts.

Unlike lubricating oils that flow of their own accord (Newtonian fluids), most greases flow only under pressure (Non-Newtonian fluid).

The fiber structure of thickener is adversely affected by water contamination and the grease undergo degradation. Hence, (unless a grease has been formulated to function), it is not used in the presence of water.

Shear or frictional resistance of Greases is much higher than oils hence they can support much heavier load at lower speed.

Coefficient of friction of greases is much higher than that of lubricating oils. Therefore, whenever possible, it is better to use an oil instead of grease.

Compared to lubricating oils, greases cannot effectively dissipate heat from the bearing. That's why the grease lubricated bearing works at relatively lower temperatures as compared to the oil-lubricated bearing.

*Preparation.* Greases are made by saponification of fat with alkali (like Caustic soda) followed by adding hot lubricating oils with constant mixing. Consistency of the finished grease is governed by the total amount of the mineral oil.

*Applications.* Greases have the following uses :

- (i) In rail axle boxes (or any other such applications where oil cannot remain in place due to high load, low speed, intermittent operation, sudden jerks etc.)
- (ii) in bearings and gears that works at high temperatures ;
- (iii) in machines preparing paper, textiles, edible articles etc. where dripping of oil is undesirable ;
- (iv) in situations where bearing needs to be sealed against entry of dust, dirt, grit or moisture, as the greases are more resistant to contamination by these agents.

**Classification of greases on the basis of the soap used in their manufacture :**

(i) *Soda-based greases* employ sodium soaps as thickening agent in petroleum oils. As the sodium soap content is soluble in water so these greases are not water resistant. These greases can be used up to  $175^{\circ}\text{C}$ . They are suitable for use in ball bearings which generates frictional heat.

(ii) *Lithium-based greases* employ lithium soaps as thickening agent in petroleum oils. These greases are resistant to water and have good high-temperature properties. These greases are stable in storage, have high mechanical and oxidation stability. They have high melting point (about  $150^{\circ}\text{C}$ ).

For aircraft applications at extreme heights, where temperature as low as  $-55^{\circ}\text{C}$  may exist, lithium-base lubricant (properly formulated) can be used as they permit functioning of the controls under such conditions. These greases are used for special applications only, due to their high cost.

(iii) *Calcium-based greases* employ calcium soaps as thickening agent in petroleum oils. These greases are also known as Cap-greases. These greases are the cheapest and most commonly used. These are water resistant and can be used up to  $80^{\circ}\text{C}$ . The amount of lime can be varied from 10 to 30% in calcium-based greases for getting wide range of consistency, from soft paste to hard, smooth solid.

These greases are suitable for lubricating caterpillar treads, tractors ; water pumps etc.

(iv) *Axle greases* are very cheap resin greases. They are prepared by adding lime (or any heavy metal hydroxide) to resin and fatty oils. After thorough mixing and standing, stiff mass grease floats out. Talc, mica or any other suitable filler is also added to them. They are resistant to water and used for equipment working at low speeds and high loads.

### 4.3 Solid Lubricants

These lubricants reduce friction by separating two moving surfaces under boundary conditions. They are used either in the dry powder form or mixed with oil or water. Low spots on the surface of moving parts are filled by these lubricants which then form solid films having low frictional resistance. The usual coefficient of friction of solid lubricants is between 0.005 and 0.01. Solid lubricants find applications in :

- (i) Commutator bushes of motors and electronic generators where contamination of grease or lubricating oil (by the entry of dust or grit particles) is unacceptable ;
- (ii) Internal combustion engines where a tight film is desired between the piston rings and the cylinder for increasing compression. In this application, combustible lubricants must be avoided. Lubricating film cannot be secured by using lubricating oils or greases because of the high operating temperatures.

The two most commonly used solid lubricants are :

- (i) Graphite. Graphite consists of number of flat plates made up of network of hexagons in which each carbon is in  $sp^2$  hybridisation state [see Fig. 7(a)]. The plates



are separated from each other by  $4 \text{ \AA}$  and are held together by weak Van der Waals' forces so that even a small force is sufficient to slide the layers parallel to each other. Hence, it has low coefficient of friction. It is very soapy to touch, non-inflammable and not oxidized in air below  $375^\circ \text{C}$ . It can be used up to very much higher temperatures in the absence of air. It is used in the powdered form or as suspension in oil or water along with tannin as emulsifying agent. Graphite dispersed in oil (termed as oildag) is used in internal combustion engines as it gives a tight-fit contact by forming a film between the piston rings and the cylinder thereby increasing compression. Graphite dispersed in water (termed as aquadag) is useful where a lubricant free from oil is needed. Graphite greases (i.e., graphite mixed with grease) is useful for higher temperature applications. Graphite is used as lubricant in air-compressors, foodstuff industry, railway track-joints, open gears, cast iron bearings, general machine-shop works etc.

(ii) Molybdenum disulphide. It has a sandwich-like structure in which a layer of molybdenum atoms lies between two layers of sulfur, which are  $6.26 \text{ \AA}$  apart, see Fig. 7(b).

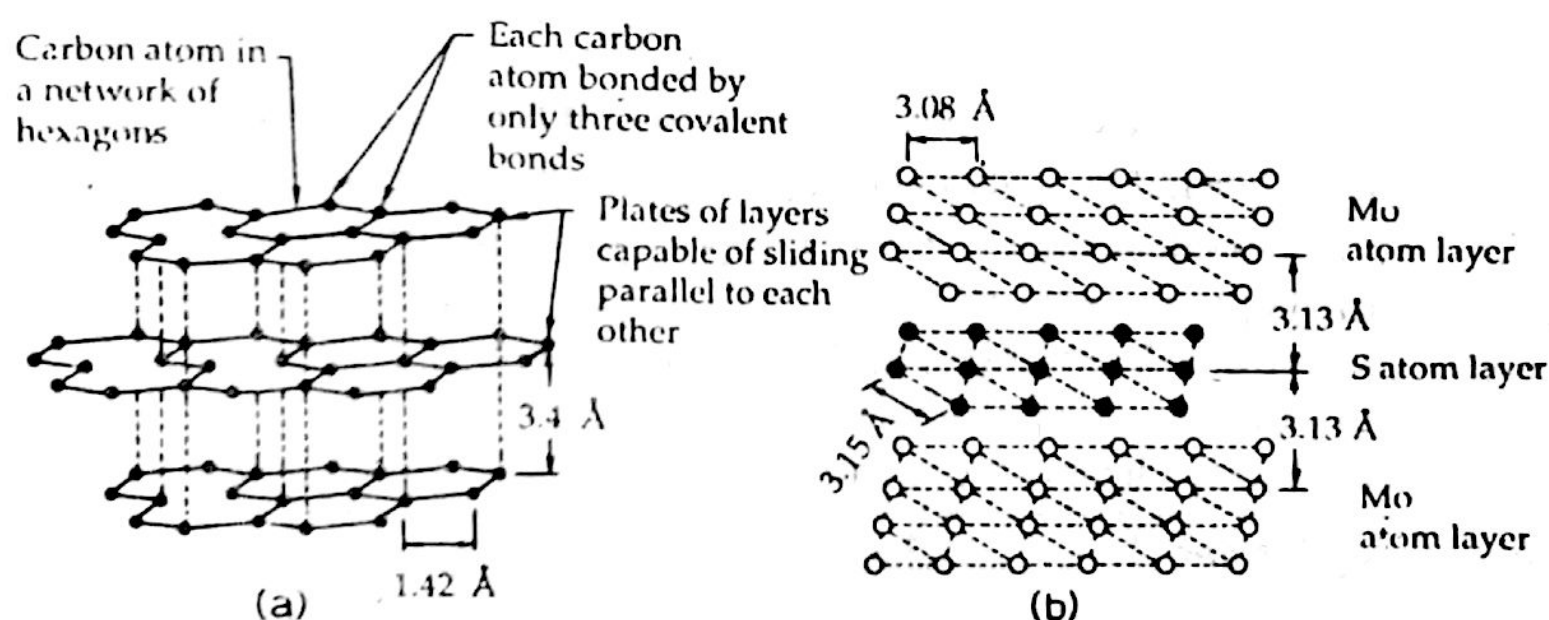


Fig. 7. (a) Layered structure of graphite : (b) Sandwich-like structure of molybdenum disulphide.

$\text{MoS}_2$  has low shear strength in a direction parallel to the layers due to poor interlaminar attraction. That's why  $\text{MoS}_2$  has very low coefficient of friction. It is stable in air up to  $400^\circ \text{C}$ . A solid-film lubricating surface useful for space vehicles is made from (70%  $\text{MoS}_2$  + 7% graphite) bonded with 23% silicates, which can withstand extreme temperatures, low pressures and nuclear radiations.

#### 4.4 Synthetic Lubricants

These are manufactured or synthesized in chemical plants or refineries (by combining, reacting or polymerizing basic components some of which may be the by-products of oil refining) to produce tailor-made products that can lubricate like conventional lubricants but at severe or extreme conditions, as they exhibit unique combinations of properties like high-temperature stability, extended temperature range, long service life even in reactive environments etc.

These lubricants are not produced directly during the normal manufacturing and refining processes of the petroleum industry.



Relative properties of synthetic lubricants after incorporating additives are summarized below :

Synthetic lubricant	Low Temperature properties	High Temperature Stability	Viscosity Index	Lubricity	Volatility	Fire-resistance	Hydrolytic stability
Polyalphaolefins (PAO)	G	G	G	G	G	P	E
Diesters	E	E	V	G	A	F	F
Linear alkyl benzenes (LAB)	G	F	P	G	A	P	E
Polyalkylene Glycols (PAGs)	G	G	E	G	G	P	G
Phosphate esters	V	E	P	G	A	E	F
Silicones	E	E	E	P	G		F
Fluorinated Lubes	F	E	E	V	A	E	E

where F = Fair, G = Good, E = Excellent, V = Varies

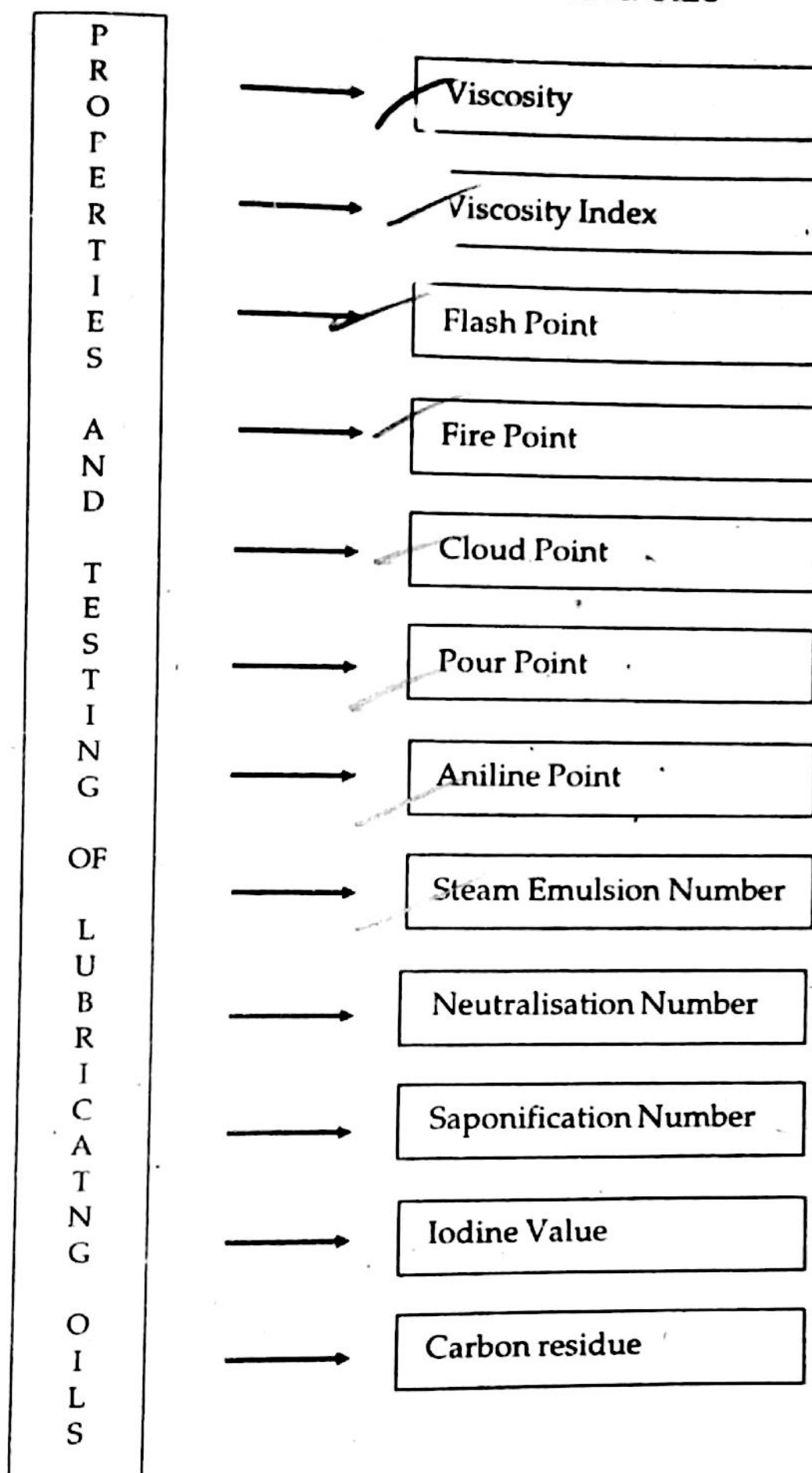
In general, synthetic lubricants possess the following properties :

- (i) Thermal stability even at high operating temperatures ;
- (ii) Chemical stability even in corrosive environments ;
- (iii) High viscosity-index ;
- (iv) non-inflammability and high flash points ;
- (v) low freezing point.

Few typical applications of synthetic lubricants are given below :

Synthetic lubricant	Application	Remarks
Di-2 ethyl sebacate (Diester)	Used for lubrication in turbo-jets	Satisfactory performance from $-50^{\circ}\text{C}$ to $230^{\circ}\text{C}$
Phosphate esters	As additive in petroleum lubricants	Improves boundary lubrication properties.
Poly alkylene glycol (PAGs)	Aircraft turbine lubricants	Thermally stable, free from corrosive action, stable even at high rates of mechanical shear.
Higher polyalkylene-oxides, polyglycidyl ethers	Residue free high temperatures lubricants for roller bearings of sheet glass machinery	Decompose into volatile parts at high temperatures.
Fluorinated lubes	Used in Submarines	Less susceptible to oxidation and cracking, high chemical and thermal stability
Silicone	Moisture-repellent dielectric lubricants for clocks, timers and other electronic devices	
	Not used for aircraft turbine lubricants	Prone to oxidize at high temperatures forming gels

## 5 PROPERTIES AND TESTING OF LUBRICATING OILS



### 5.1 Viscosity

*Viscosity* is the property of a fluid that determines its resistance to flow. It is an indicator of flowability of a lubricating oil, the lower the viscosity, greater the flowability. It is mainly due to the forces of cohesion between the molecules of lubricating oil.

*Absolute viscosity* may be defined as "the tangential force per unit area which is required to maintain a unit velocity gradient between two parallel layers. It is denoted by  $\eta$  ( $\eta$ ). Its unit in C.G.S. system is poise and its dimensions are  $ML^{-1}T^{-1}$ .

*Absolute Kinematic viscosity* is the ratio of absolute viscosity to density for any fluid. It is denoted by  $\nu$ . Its unit in C.G.S. system is stokes and its dimensions are  $L^2T^{-1}$ .

### Effect of temperature on viscosity

Like any other fluid, viscosity of lubricating oil is inversely proportional to temperature. *i.e.*, with increase of temperature, viscosity decreases. This is due to the decreases in intermolecular attraction.

At higher temperatures, oils must have sufficient viscosity to carry loads. Hence, heavier oils are used at higher temperatures. Similarly, light oils are used at low ambient temperatures.

### Effect of pressure on Viscosity

Lubricating oils are subjected to extreme pressure at the interface between gears and between rolling element and race in a rolling bearing. At such high pressures, viscosity of lubricating oils increases considerably.

### Significance of Viscosity

*Viscosity helps in the selection of good lubricating oil.* For instance, *Light oils* have low densities and easy flowabilities. These oils *i.e.*, generally used on parts moving at high speed promotes the formation of a good oil film. Moreover, light oils do not impose much drag on high-speed parts, see Fig. 8.

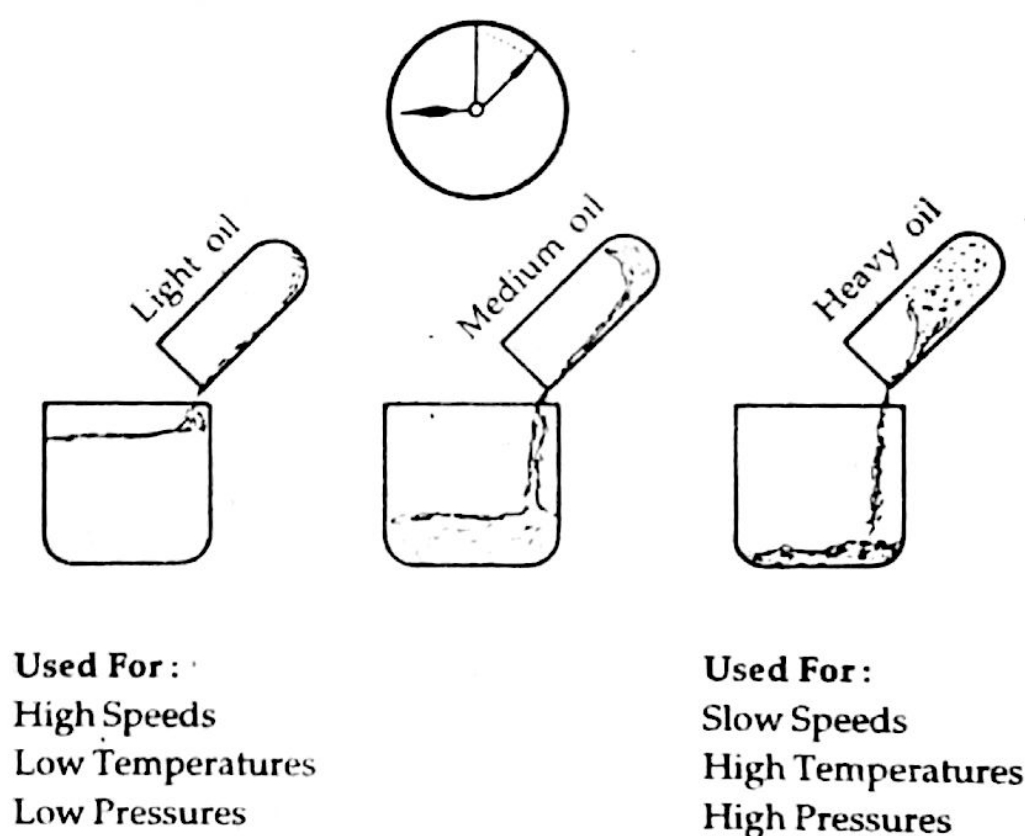


Fig. 8. Viscosity

In contrast, *Heavy oils* are used on parts moving at slow speed under heavy loads as they resist being squeeze out. Light oils are not suitable in this case as they have low viscosities and it is not possible to maintain lubricant film between the moving surfaces. Subsequently, excessive wear will occur.

To sum up, in hydrodynamic lubrication, that lubricant is selected which should have a sufficient high viscosity to adhere to the bearing and resist being squeeze out due to high pressure and get fluid enough to resist excessive friction due to the shearing of oil itself. Thinner oil can easily dissipate the frictional heat because of good oil circulation.

### 5.2 Measurement of viscosity of a lubricating oil

There are many instruments for measuring viscosity and are known as viscometers (or viscositymeters). For examples, kinematic & saybolt universal viscometers are used in the United States and the Redwood viscometers are commonly used in England.



### The Saybolt Viscometer

It consists of a cylindrical brass cup in the bottom of which is an orifice of specified dimension. This cup is surrounded by a constant temperature oil bath. A desired bath temperature can be obtained by adjusting the temperature regulator. It is shown in Fig. 9. When the sample of lubricating oil reaches test temperature, the time required for 60 mL of the oil to run through the orifice is measured. The oil sample flows by gravity under a standard falling head and at a temperature of 100° F and 210° F. A calibrated standard flask collects the liquid sample. The time of efflux is measured in seconds and are reported as Saybolt Universal Seconds (SUS); for example, 260 SUS at 100° F.

For heavy lubricating oils with high viscosities, a larger orifice is used in the same apparatus, and the results are reported in Saybolt Furol Seconds (SFS) at a specified temperature.

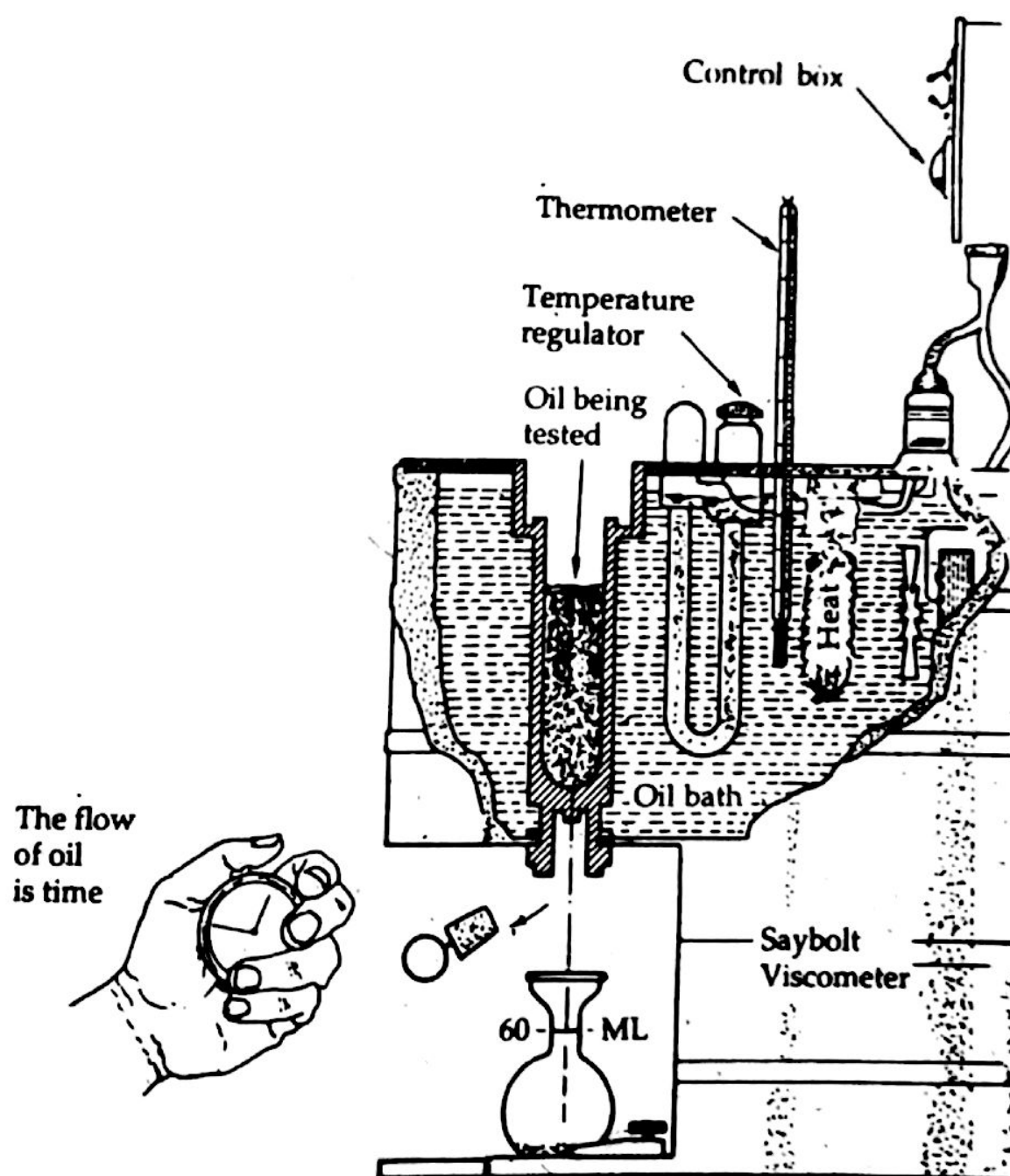


Fig. 9. Saybolt viscometer.

### The kinematic Viscometer

It is a U-type of glass apparatus having respectively one and two bulbs at its two sides. At the bottom portion of two bulb side, capillary tube is attached. It is

used for the determination of Kinematic viscosity. The four simple measurement steps are shown in Fig. 10.

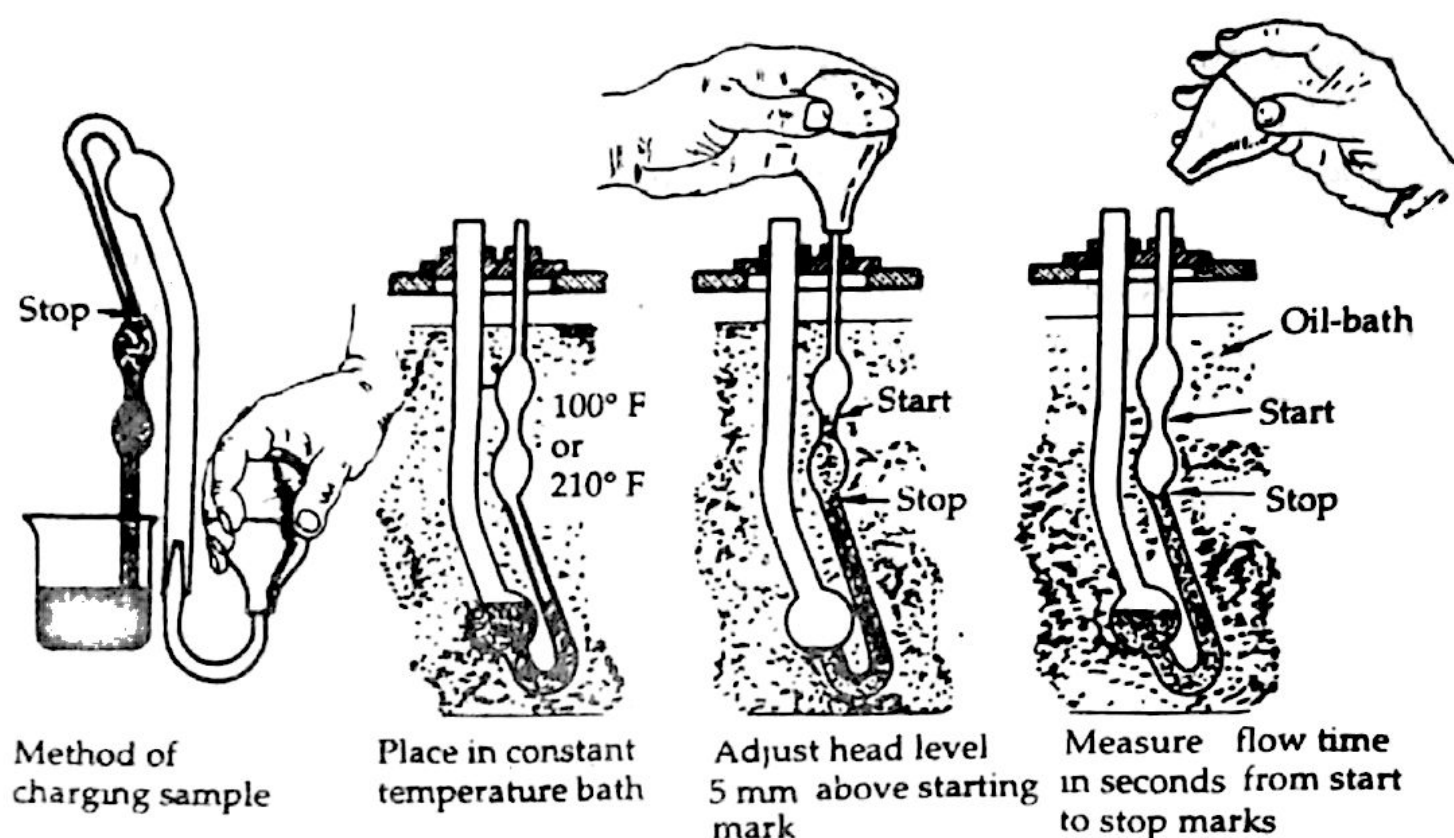


Fig. 10. The kinematic viscometer.

For a fixed volume of sample, time is measured for the sample to flow through a calibrated capillary under an accurately reproducible head of liquid and at a constant temperature. From the measured efflux time, the kinematic viscosity is calculated.

Kinematic viscosity in centistokes (cSt) =  $C \times t$

where  $C$  = Viscometer constant and

$t$  = Observed flow time in seconds.

#### The Redwood Viscometer

It is of two types :

(a) Redwood viscosity No. 1—Universal and (b) Redwood viscosity No. 2-Admiralty.

The essential differences between the two are :

	(a)	(b)
<i>Dimensions of orifice</i>	Length-10 mm	50 mm
	Diameter-1.62 mm	3.80 mm
<i>Receiving flask has</i>	Smaller mouth	Larger mouth
<i>Useful for</i>	Low Viscous Oil	Higher Viscous Oil

The Redwood No. 1 apparatus consists of a cylindrical brass oil cup (90 mm in height and 46.5 mm in diameter) that holds the test sample of lubricating oil. The

bottom of the oil cup is fitted with a polished-agate discharge tube containing an orifice of specified dimension. The oil cup is surrounded by water bath for adjusting the temperature. A calibrated receiving flask (known as Kohlrausch flask) is provided for receiving the oil from polished-agate discharge tube. It is shown in Fig. 11. When the sample reaches test temperature the time for 50 mL of the sample to flow through the orifice is measured. Results are reported in seconds, stating the test temperature and viscometer.

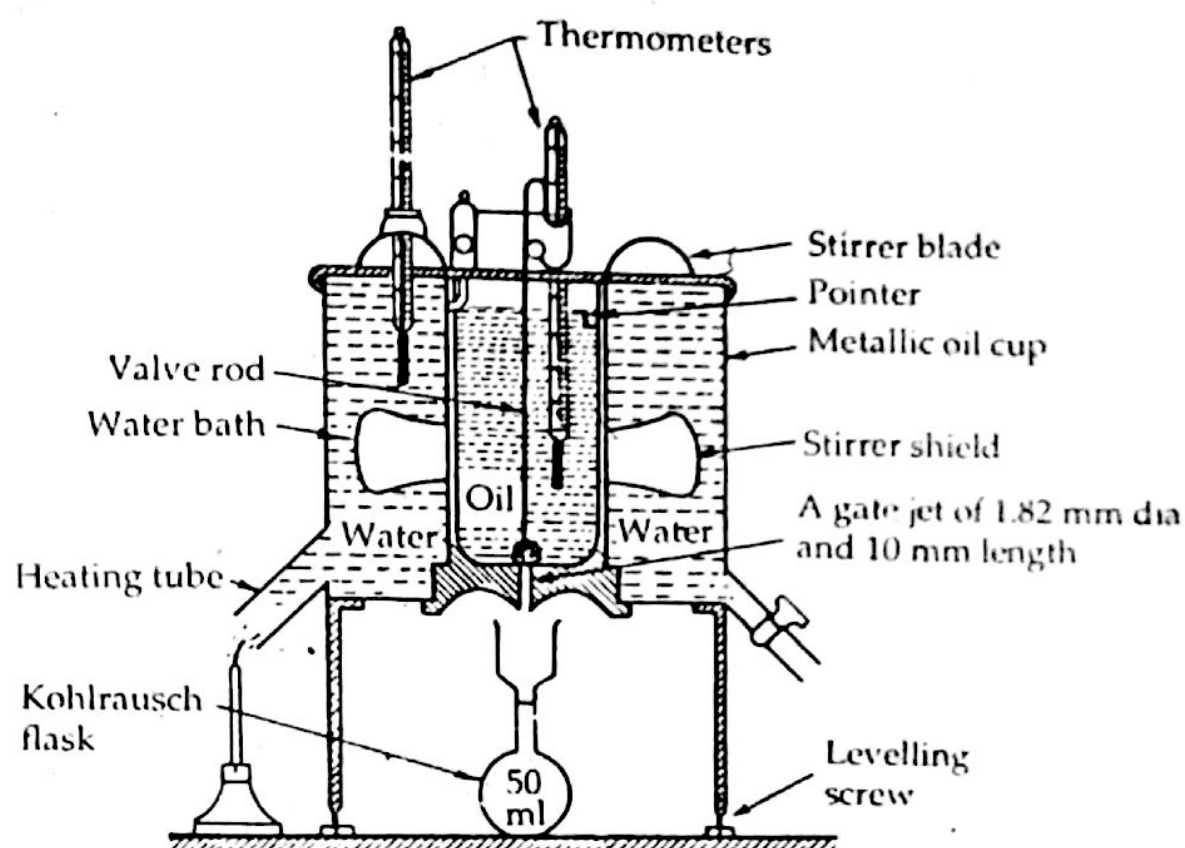


Fig. 11. Redwood viscometer No. 1.

For example, Redwood viscosity No. 1 at 140° F, 350 seconds.

#### Conversion Formulas

Let time of efflux =  $t$  seconds,

$$\text{Saybolt} : c S t = 0.22 t - 180/t$$

$$\text{Redwood} : c S t = 0.26 t - 171/t$$

#### Significance of viscosity measurements

Viscosity is the property of a lubricating oil that determines its ability to lubricate. Viscosity values are used in evaluating load carrying capacity, in denoting the effect of temperature changes, for establishing uniformity in shipments and for determining the presence of contaminants in used oil during service. Absolute viscosity values are required for use in all bearing design calculations and other lubrication engg. technical design problems. Kinematic values are applied in oil blending procedures.

#### 5.3 Viscosity Index

With changes in temperature, the viscosity of lubricating oil varies, the higher the temperature, the lower the viscosity and vice-versa. The rate of variation of viscosity with temperature is different for different base oils or fluids. For example, in petroleum oils, the viscosities of naphthenic base oils vary more over the same



temperature range than those of paraffinic base oils. The rate at which the viscosity of an oil changes with temperature is measured by an empirical number known as the viscosity-index (V.I.). A relatively small change in viscosity with temperature is indicated by high viscosity index. Whereas a low viscosity index shows a relatively large change in viscosity with temperature. The pennsylvanian oils, consisting mainly of paraffins, are arbitrarily assigned a viscosity index value of 100 as they exhibit a relatively small change in viscosity with a rise in temperature. Oils of Gulf-coast origin, consists mainly of alicyclics (naphthenes), are arbitrarily assigned a viscosity index value of 0 as they exhibit a larger change in viscosity with a rise in temperature. In industry, lubricating oils of high viscosity index are preferred since they have practically the same viscosity over a range of temperatures.

### Determination of Viscosity-index

Viscosity index of test oil is determined with the help of two types of standard oils viz. Pennsylvanian oils and Gulf oils having V.I.'s 100 and 0 respectively.

The V.I. of the test oil is given by the formula

$$V.I. = \frac{L - U}{L - H} \times 100$$

where V.I. = viscosity index of the oil under-test

$L$  = viscosity at 100° F of the low-viscosity standard oil having a V.I. of 0 (i.e., Gulf oil) and also having the same viscosity as the oil under test at 210° F

$U$  = Viscosity at 100° F of the oil under test.

and  $H$  = viscosity at 100° F of the high-viscosity standard oil having a V.I. of 100 (i.e., Pennsylvanian oil) and also having the same viscosity as the oil under test 210° F.

**Example 1.** An oil of unknown viscosity-index has a saybolt universal viscosity of 60 seconds at 210° F and of 600 seconds at 100° F. The high viscosity index standard (i.e., Pennsylvanian) oil has Saybolt viscosity of 60 seconds at 210° F and 500 seconds at 100° F. The low viscosity-index standard (i.e., Gulf) oil has a saybolt universal viscosity of 60 seconds at 210° F and 800 seconds at 100° F. Calculate the viscosity index of unknown oil.

**Solution.** Here  $L = 800$  s,  $H = 500$  s and  $U = 600$  s

$$\begin{aligned} \text{So, viscosity-index of unknown oil } V.I. &= \frac{L - U}{L - H} \times 100 \\ &= \frac{800 - 600}{800 - 500} \times 100 = \frac{200}{300} \times 100 \\ \Rightarrow V.I. &= 66.67 \end{aligned}$$

**Example 2.** An oil sample under test has a saybolt universal viscosity of 64 seconds at 210° F and 564 seconds at 100° F. The low viscosity standard (Gulf oil) possesses a saybolt viscosity of 64 seconds at 210° F and 774 seconds at 100° F and 414 seconds at 100° F. Calculate the viscosity-index of the oil sample under test. (Bhopal I B.E., 2001)

**Solution.** Here,  $L = 774$  s,  $H = 414$  s and  $U = 564$  s

So, viscosity-index of the oil-sample under test,  $V.I. = \frac{L - U}{L - H} \times 100$

$$\Rightarrow V.I. = \frac{774 - 564}{774 - 414} \times 100 = 58.33$$

**Example 3.** An oil sample under-test has a Saybolt Universal Viscosity same as that of standard Gulf oil (low Viscosity Standard) and Pennsylvanian oil (high viscosity index standard) at 210° F. Their Saybolt Universal viscosities at 100° F are 61, 758 and 420 s respectively. Calculate viscosity-index of the sample oil.

**Solution.** Here,  $L = 758$  s,  $H = 420$  s, and  $U = 61$  s

So, viscosity-index of the sample oil  $V.I. = \frac{L - U}{L - H} \times 100$

$$\Rightarrow V.I. = \frac{758 - 61}{758 - 420} \times 100 = 206.2$$

### Viscosity Index and Molecular Structure of Oil

There is a direct co-relation between molecular structure of lubricating oil with its viscosity and viscosity-index.

A high V.I. is exhibited by those lubricating oils which have linear or rod-like shaped molecules of higher molecular weights. This is due to the greater inter-molecular attraction.

### Viscosity-Temperature Curves

the variation of viscosity with temperature can also be indicated by viscosity-temperature curves. In fact, viscosity index is the numerical expression of the average slope of the viscosity-temperature curve of a lubricating oil between 100° F and 210° F. Lubricating oils with small variation in viscosity with temperature exhibit flatter viscosity-temperature plots and they have high VI's.

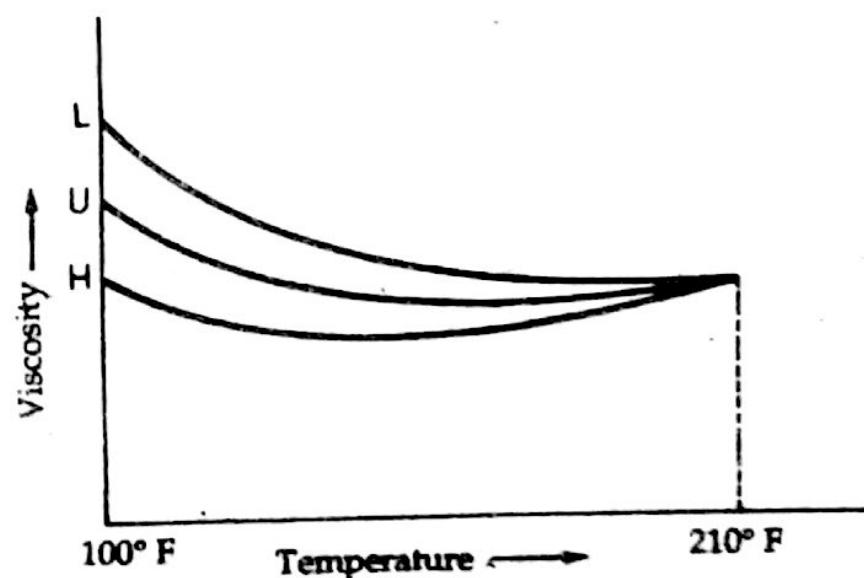


Fig 12. Viscosity-temperature curve.

### 5.4 Flash and Fire Point

(The flash point of an oil is the lowest temperature at which it gives off vapours that will ignite for a moment when a small flame is brought near it.)

The fire point of an oil is the lowest temperature at which the vapours of the oil burn continuously for at least 5 seconds when a small flame is brought near it.

The flash points and fire points are used to indicate (the fire hazards of petroleum products and evaporation losses under high temperature operations.)

Knowledge of flash and fire points in lubricating oil aids in precautionary measures against fire hazards. A good lubricant should have flash point at least above the temperature at which it is to be used.

### Measurement of Flash and Fire Points of a Lubricating Oil

(i) *Cleveland open cup method.* By this method we can determine the flash and fire points of all petroleum products except fuel oils and those having an open-cup flash below  $175^{\circ}\text{F}$ . It essentially consists of an open brass cup known as cleveland flash cup which is supported over the circular opening of a heating plate as shown in Fig. 13. Gas burners or electric heaters can act as a source of heat. A thermometer ( $-6^{\circ}$  to  $400^{\circ}\text{C}$ ) is also required for measuring flash and/or fire point of lubricating oil.

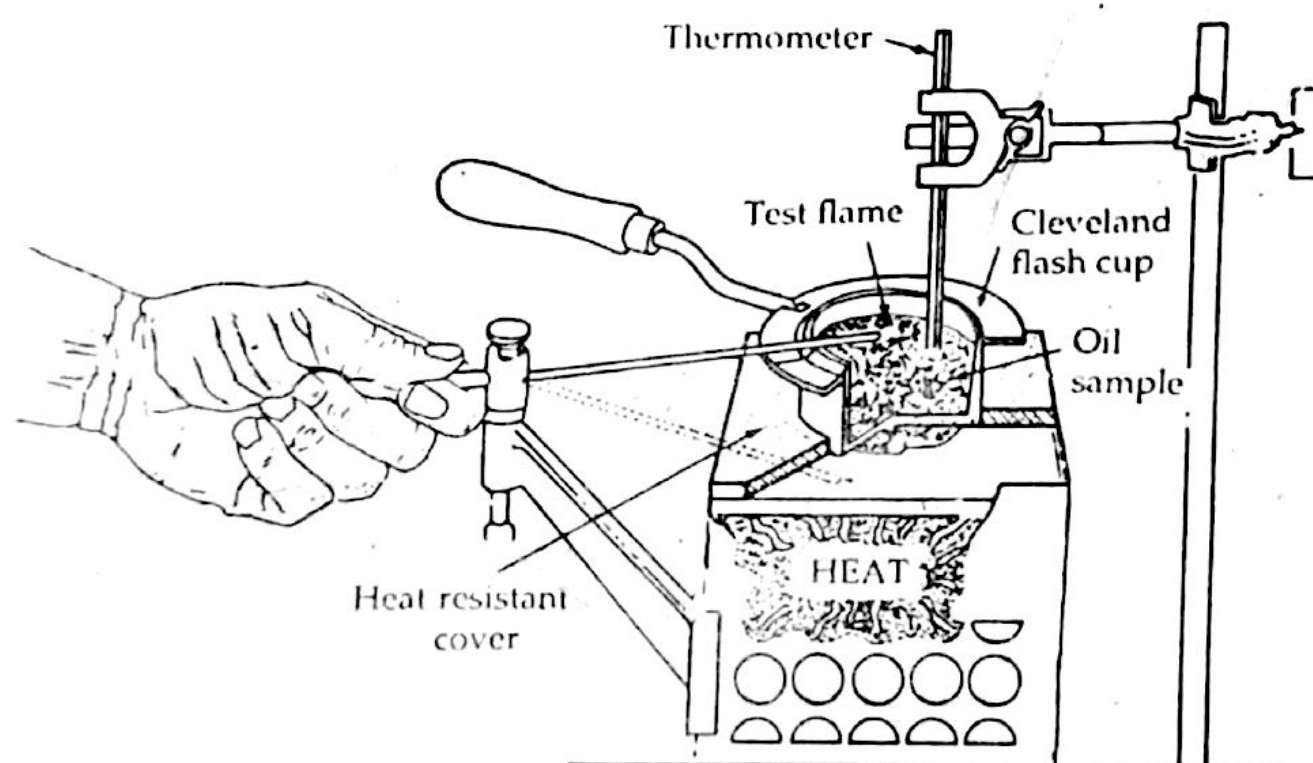


Fig 13. Cutaway view of cleveland open flash cup.

*Procedure.* The cleveland cup is filled with oil sample to be tested up to the specified filling mark. There should be no oil on the outside of the cup. The thermometer is immersed in the sample which is then heated at a rate of  $9^{\circ}$  to  $11^{\circ}\text{F}$  per minute.

At every  $5^{\circ}\text{F}$  rise in temperature a small flame is passed over the oil surface. When a flash appears at any point on the surface of the oil, the temperature reading shall be reported as the *flash point*. The heating of the oil is continued at the same rate. The test flame is applied again for every  $5^{\circ}\text{F}$  rise in temperature until oil ignites and continues to burn for at least 5 s. The temperature reading is recorded as the *fire point*. Fire point range from  $10^{\circ}$  to  $70^{\circ}\text{F}$  higher than the flash point.

*Limitation.* The flash point of lubricating oil should be greater than  $175^{\circ}\text{F}$ .

(ii) *The Pensky-Marten Closed cup method.* It is used to determine the flash point of lubricating oils, fuel oils, solvents, solvent containing materials and suspension of solids, except cut-back asphalt.

It consists of a cup made of brass, which is about 5.5 cm deep and 5 cm in diameter. The lid of the cup is provided with four openings of standard sizes.



Through one of these openings passes a *stirrer* carrying two brass blades ; while the second opening is meant for admission of air. Through third opening passes a thermometer. While the fourth is meant for introducing test flame.

At the top of the cup, a *shutter* is provided. By moving the shutter, opening in the lid opens and flame (from *flame exposure device*) is dipped into this opening, thereby bringing the flame over the oil surface. As the test-flame is introduced in the opening, it gets extinguished, but when the test-flame is returned to its original position, it is automatically lighted by the pilot burner. There is also a stove consisting of an air bath and a top plate on which the flange of the cup rests. The air bath may be either a flame-heated metal casting or an electric-resistance element. Penskey-Marten's flash point apparatus is shown in Fig. 14(a).

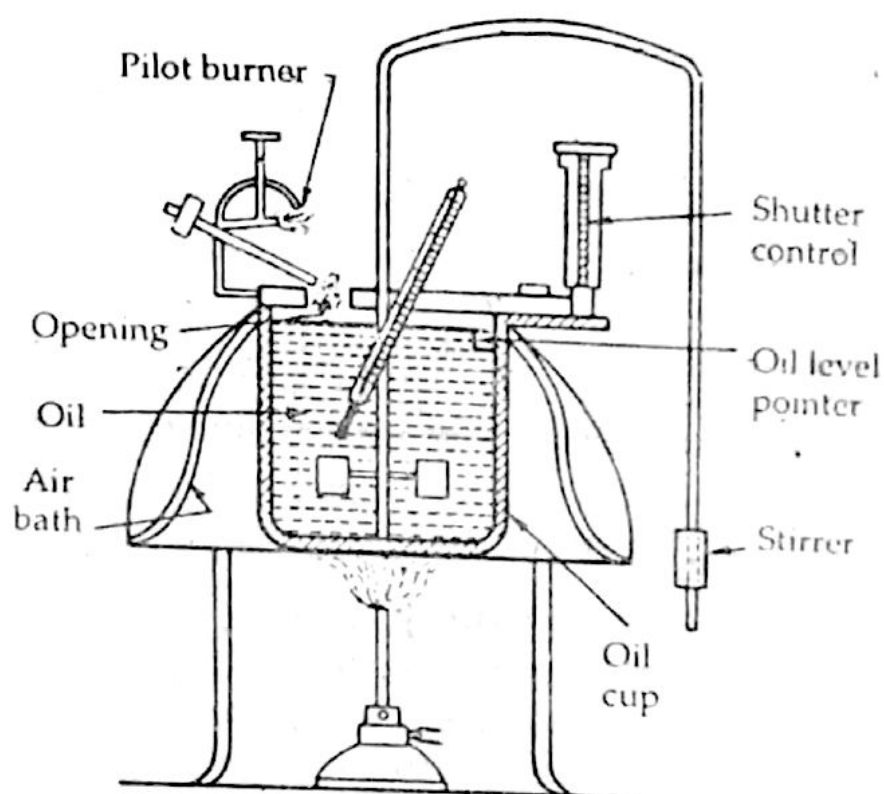


Fig. 14. (a) Penskey-Marten's flash point apparatus.

*Procedure.* The oil sample is filled up to the specified filling mark in the cup. It is then covered and positioned properly in the stove. The thermometer is inserted in the sample. The test flame is lighted, while being stirred, the sample is heated at

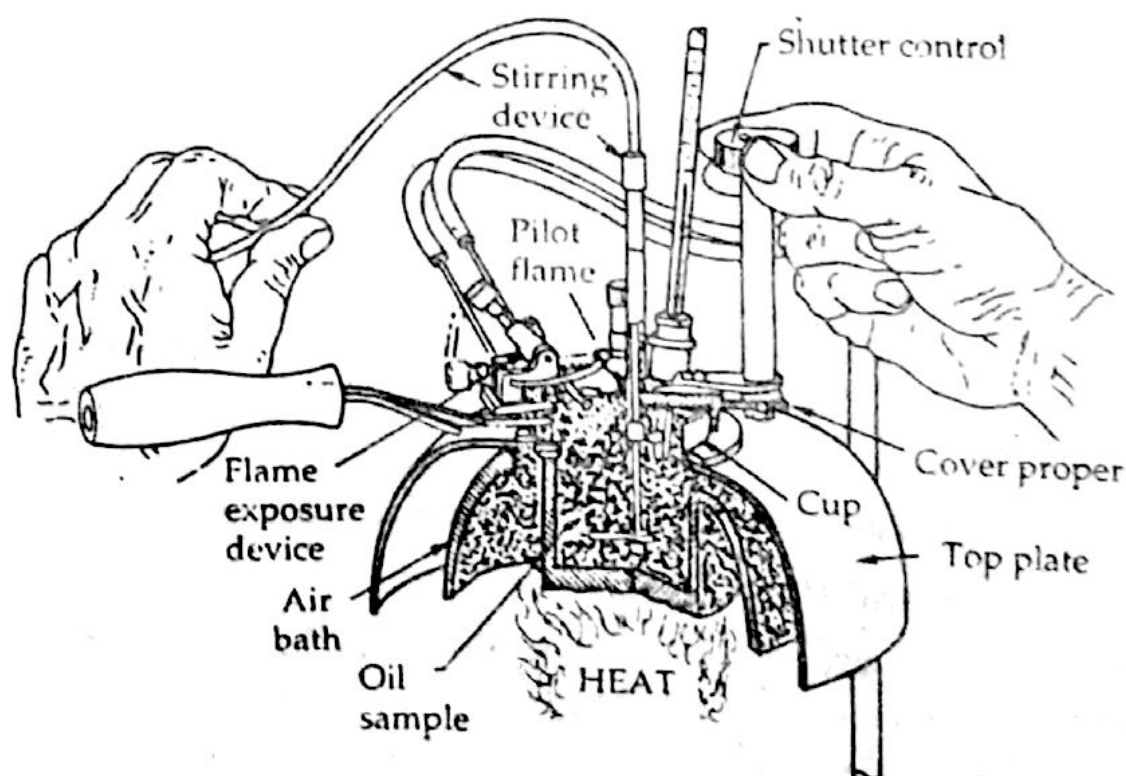


Fig. 14. (b) Cutaway view of Penskey-Marten's flash point apparatus.

the rate of  $9^{\circ}$  to  $11^{\circ}$  F per minute. Upto  $220^{\circ}$  F, the test flame is applied at every  $2^{\circ}$  F rise in temperature, thereafter it is applied at every  $5^{\circ}$  F rise in temperature. When a distinct flash occurs in the interior of the cup at the time of the flame application, the temperature reading on the thermometer is the flash point.

### 5.5 Cloud And Pour Points

The *cloud point* of a petroleum oil is the temperature at which solidifiable compounds, like paraffin wax, present in the oil begin to crystallize or separate from solution. Fig. 15(a) when the oil is cooled under specified conditions. Naphthenic type of oils that are quite wax-free show no cloud points.

The *pour point* of a petroleum oil is the temperature at which the oil ceases to flow or pour, see Fig. 15(b).

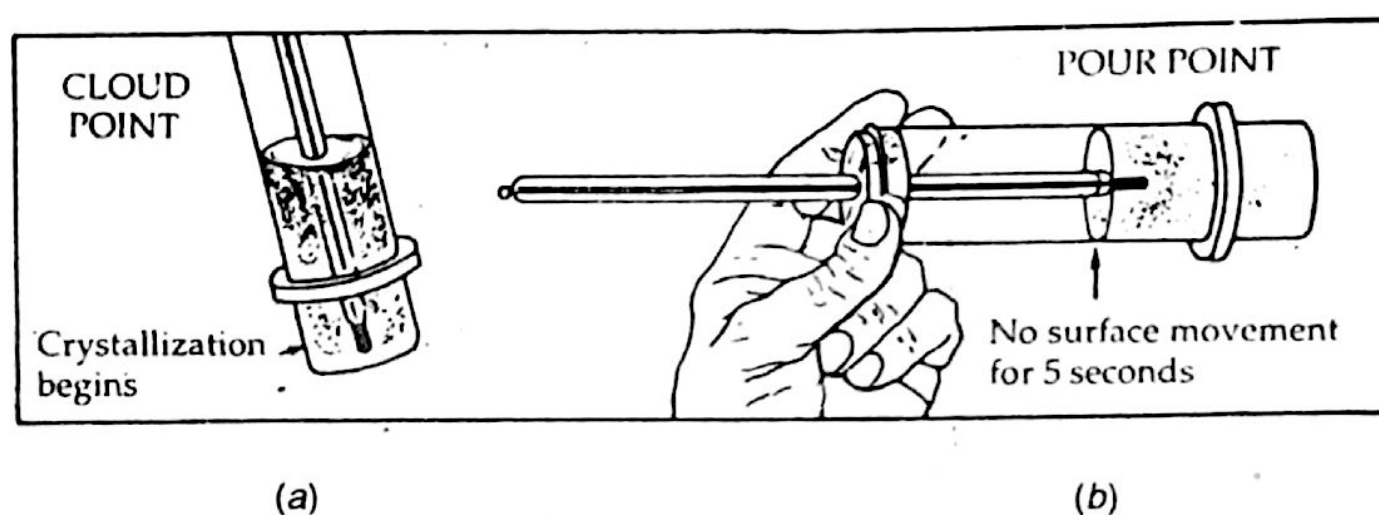


Fig. 15. Cloud and Pour points.

At the Cloud point, oil becomes cloudy or hazy in appearance. Cloud and pour-points indicate the suitability of lubricants in cold conditions. Lubricants used in a machine working at low temperature should possess low pour-point; otherwise solidification of lubricant will cause jamming of the machine, see Fig. 16. Pour point is of importance in establishing the lowest temperature at which a diesel fuel is still sufficiently fluid to be pumped or transferred. An oil with a low pour point should be selected whenever the oil must remain fluid at low temperatures.

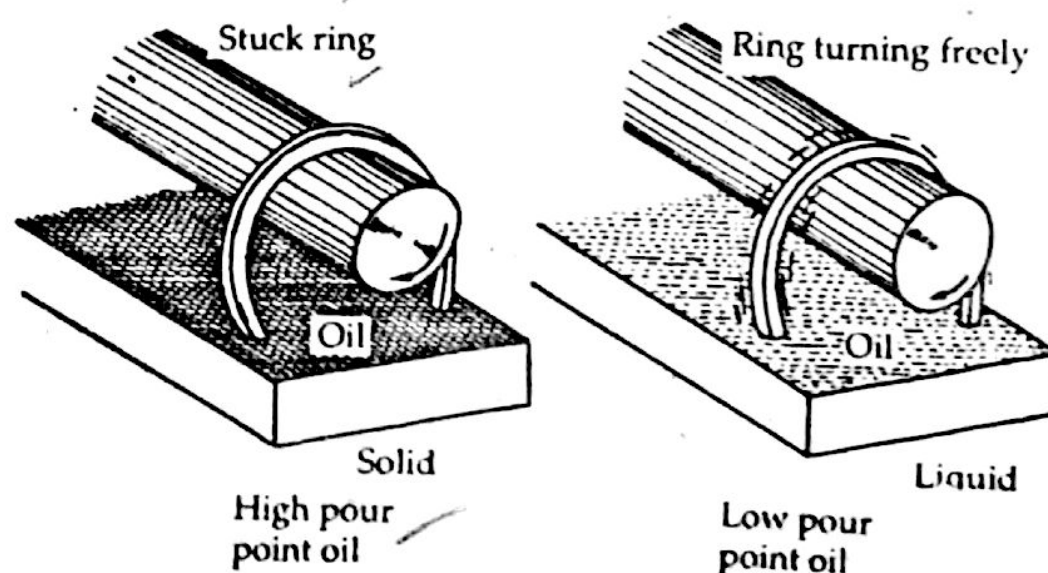


Fig. 16. Pour Point (Temperature at which the oil will cease to flow).

### Determination of Cloud and Pour Points

These determinations are carried out with the help of apparatus shown in Fig. 17. The apparatus consists of a flat-bottomed tube (about 2 cm high and 3 cm in dia) enclosed in an air-jacket. The air-jacket is surrounded by freezing mixture (ice + NaCl) contained in a jar.

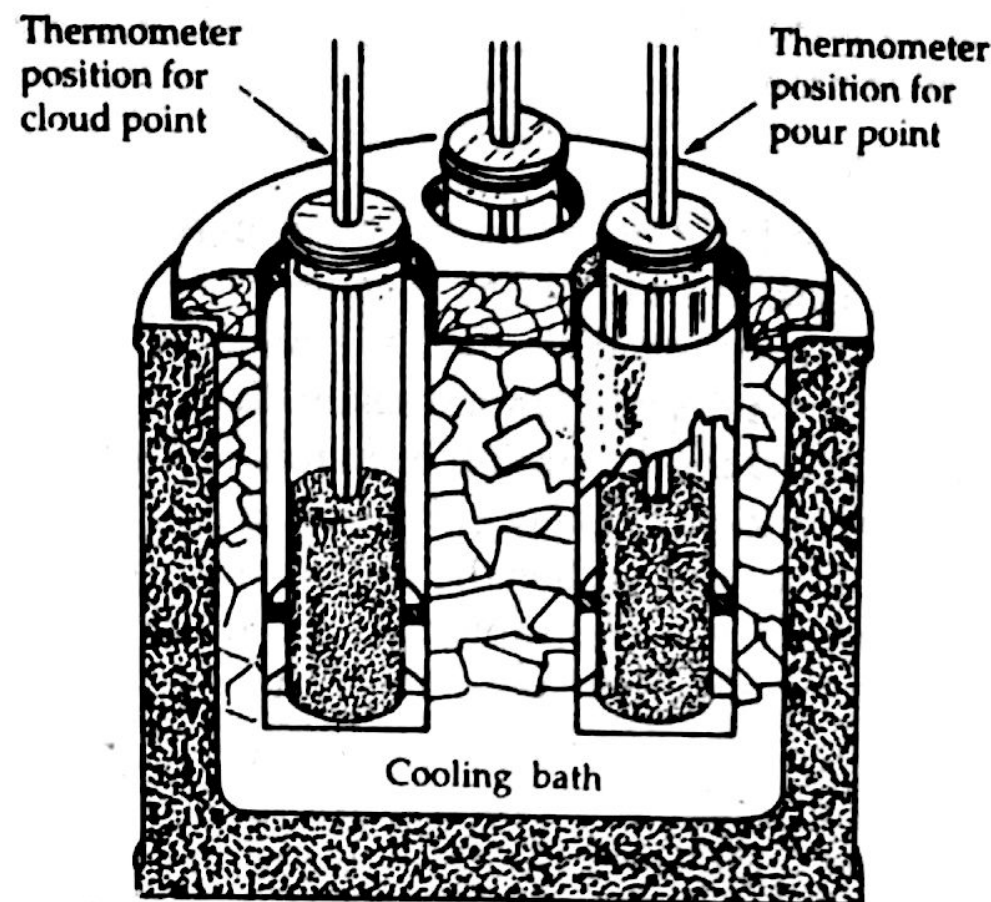


Fig. 17. Apparatus for cloud and pour points determination.

To determine *cloud point*, a sample of the lubricating oil (moisture free) is poured into a test jar and cooled in progressive steps. When inspection first reveals a distinct cloudiness or haze at the bottom of the test jar, the temperature is recorded as the cloud point.

To determine *pour point*, a sample of oil is cooled in flat-bottomed tube (*i.e.*, test jar) under specified conditions ; the temperature is observed in increments of  $5^{\circ}\text{F}$  until no movement is observed at the surface of the oil when the tube is held in a horizontal position for 5 seconds. This temperature is recorded as the solid point. By definition the pour point is  $5^{\circ}\text{F}$  above this temperature.

**Significance.** Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines might become clogged because of wax separation. Filterability depends on type of wax, micro crystalline or amorphous. The amorphous wax is sticky in nature and would more easily clog filter screens.

Pour point values of petroleum and non-petroleum lubricants are significant as many operations must function in sub-freezing conditions.

### 5.6 Aniline Point

Aniline point is defined as "the minimum equilibrium solution temperature for equal volume of aniline and oil sample." It is determined by thoroughly mixing equal volumes of oil sample and aniline in a test tube and heating the mixture until a homogeneous solution is obtained. Then, the tube is allowed to cool at a controlled rate. The temperature at which the oil and aniline phases separate out is recorded as the *aniline point*. A lower aniline point of an oil means a higher percentage of aromatic hydrocarbons in it. Since aromatic hydrocarbons have a tendency to-dissolve natural rubber and certain types of synthetic rubbers. Thus, higher the percentage of aromatic hydrocarbon or lower the aniline point of a oil,



more are the chances of deterioration of an oil when it comes in contact with rubber sealings, packing, etc. Consequently, low aromatic content in the lubricants or their higher aniline point is desirable.

### 5.7 Steam Emulsion Number

When water enters an oil system, as it often does in hot strip mills, turbulence caused by high volume flow results in the formation of emulsions and initiate mixture of oil and water. Depending on the base oil and the refining processes, some oils form emulsions with water more easily than others. Moreover, contamination also contributes to the formation of emulsions. These emulsions have poor lubricating properties thereby causing abrasion and wearing out of the lubricated parts of the machinery. The higher the percentage of water, the worse the lubricating properties. Hence, it is desirable that the lubricating oil should form such an emulsion with water which breaks off readily.

This ability of lubricating oil to separate from water is called demulsibility. Oil that separates readily from water has good demulsibility (see Fig. 18), oil that does not has poor demulsibility. The tendency of lubricant water emulsion to break is determined by following test; steam at  $100^{\circ}\text{C}$  is bubbled through a test tube containing 20 mL of oil, till the temperature increases to  $90^{\circ}\text{C}$  and the time is noted when the oil and water separate out in distinct layers. The time in second in which oil and water emulsion separate out in distinct layers is called 'steam emulsion number' (SEN) or 'demulsification number'. The quicker the oil separates out from the emulsion, the lower the steam emulsion number and the better the lubricating oil for most purposes.

#### WATER SEPARATION

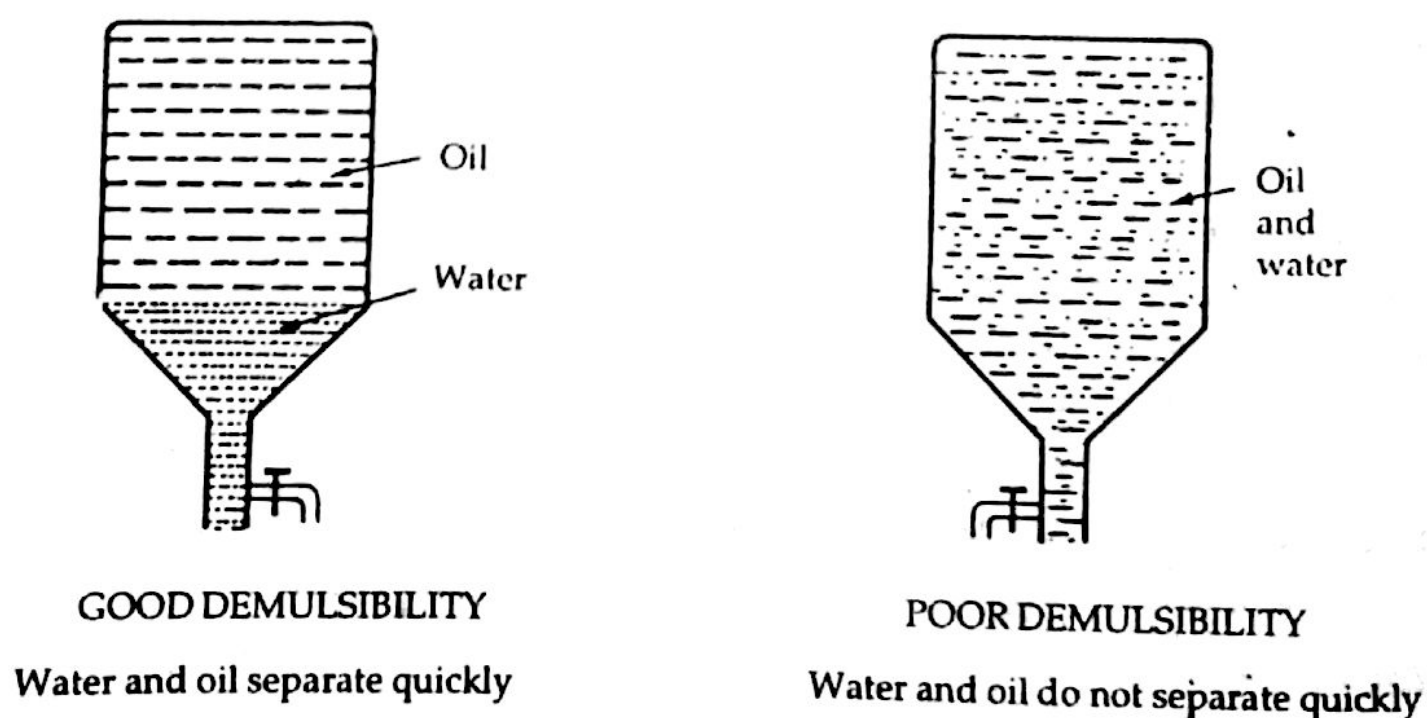


Fig. 18. Demulsibility

**Importance of the test.** To avoid corrosion of polished steel surfaces like roll necks and to ensure proper lubrication, it is important to evaluate the speed of water and oil separation (demulsibility properties) of medium to high viscosity circulating oils used in rolling mills subject to cooling water contamination.

### 5.8 Neutralisation Number

Lubricating Oil's acidity or alkalinity is determined in terms of neutralization number. The neutralization number represents either the *Total Acid Number (TAN)*

"The number of milligrams of potassium hydroxide (KOH) needed to neutralize any acid in one gram of oil" or the *Total Base Number* (TBN) The number of milligram of hydrochloric acid (HCl) needed to neutralize any base in one gram of oil. Determination of TAN is more common and its test procedure is given below :

*Reagents :*

- (i) 0.1 N alcoholic HCl solution,
- (ii) 0.1 N alcoholic KOH solution,
- (iii) Titration solvent : Made by mixing 500 mL of toluene and 5 mL of distilled water with 495 mL of isopropyl alcohol.
- (iv) Para-Naphtholbenzene indicator solution made by adding 1 g of dry indicator powder in 100 mL of isopropyl alcohol.

*Test procedure :*

- (i) Into 300 mL conical flask, take a weighed amount of the sample (20 gm sample for light-colored oil or 2 gm sample for dark-colored oil).
- (ii) Add 100 mL of titration solvent and 30 drops of indicator solution to the flask, then carefully swirl the mixture until the sample is completely dissolved.

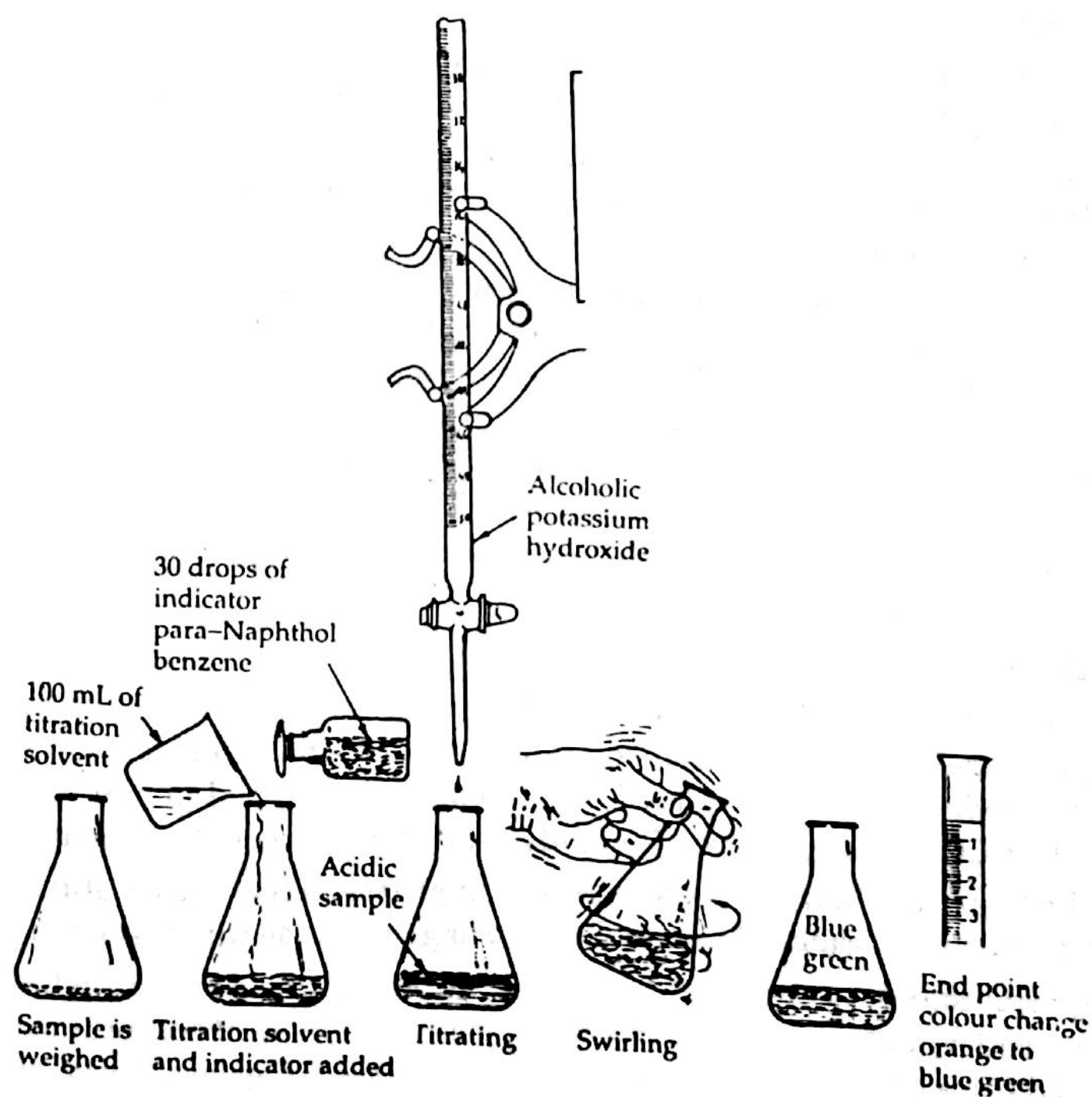


Fig. 19. Determination of Total acid number (TAN).

- (iii) If the solution turns yellow-orange or deep orange in colour, it means the oil sample was acidic [But if it assumes green or green-blue colour, it means the oil sample was basic, then titration should be done with alc. HCl].
- (iv) Slowly add the alc. KOH solution from the burette drop by drop with careful swirling until the green or green-blue end point is reached which persists for at least 15 s [The colour change is reversed if alc. HCl is the titrating agent].
- (v) Read from the burette the number of mL of solution required to reach the end point.

Calculations. Neutralization number = 
$$\frac{\text{Total mL of titrating solution} \times 5.61}{\text{Weight of sample used}}$$

**Significance.** This test shows relative changes in an oil due to oxidation. Comparing the TAN or TBN with the values of a new oil will indicate the development of harmful products or the effect of additive depletion. In fact, acid number greater than oil is usually taken as an indication of oxidation of the oil. This will, consequently lead to corrosion, besides gum and sludge formation.

### 5.9 Saponification Number

**Saponification\* number** is defined as "The number of milligrams of potassium hydroxide required to saponify the fatty material present in one gram of the oil".

**Determination.** Saponification number is determined by refluxing a known quantity of oil with a known excess of potassium hydroxide solution and titrating the unused alkali against an acid.

**Significance.** Mineral oils do not undergo saponification but animal and vegetable oils undergo saponification. Hence, this test gives an indication of the amount of animal and vegetable oils added to mineral oils to improve oiliness. Moreover, most of the animal and vegetable oils possess their own characteristic saponification values. Any deviation from this value in a given sample indicates the probability and extent of adulteration. And last but not the least, this test helps us to ascertain whether the oil under study is animal/vegetable or mineral or compounded oil.

### 5.10 Iodine Value

The **iodine value** is defined as "the number of milligrams of iodine absorbed by one gram of the oil". It is determined by the addition of a measured excess of a solution of iodine bromide in glacial acetic acid, to a weighed quantity of a oil dissolved in  $\text{CCl}_4$  or acetic acid. The addition of the halogenating agent to the double bond (s) is allowed to proceed to completion. The unused IBr is then back-titrated against standard hypo solution using starch as indicator.

**Importance.** The iodine value is a measure of the degree of unsaturation and hence the tendency of a fatty oil to absorb oxygen. Regardless of composition, any oil exposed to air and heat eventually combines with the oxygen in the air to form

\* Saponification is the alkaline hydrolysis of ester (generally of fats or oils) to give alcohol and soap (Sodium or potassium salts of higher fatty acids).



chemical compounds unsuitable for use as lubricants. Acids and gummy sludges are typical products of oxidation. Oils with high resistance to oxidation should be used in steam turbines and other large circulating oil systems, in which oils attain high temperatures and remain in service for extended duration. Oils with lower oxidation resistance are satisfactory in application (like Drop-feed oiled bearing) where oil remains in service for periods or where makeup is high because of losses.

### 5.11 Carbon Residue

Lubricating oils contain high % of carbon in combined form. On being subjected to high temperatures, they decompose and form a carbonaceous deposit. There are two methods for measuring the amount of carbon residue or deposit remaining after a lubricating oil has been subjected to extreme heat.

(i) *The Couradson method.* It is conducted in the absence of air and is applicable for heavy residuals, crudes and non-volatile stock.

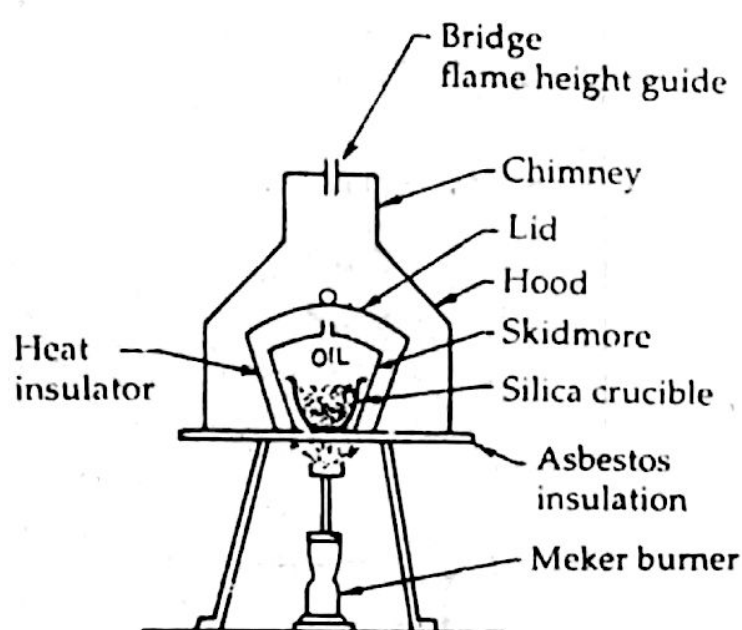


Fig. 20. (a) Couradson's apparatus for carbon residue estimation.

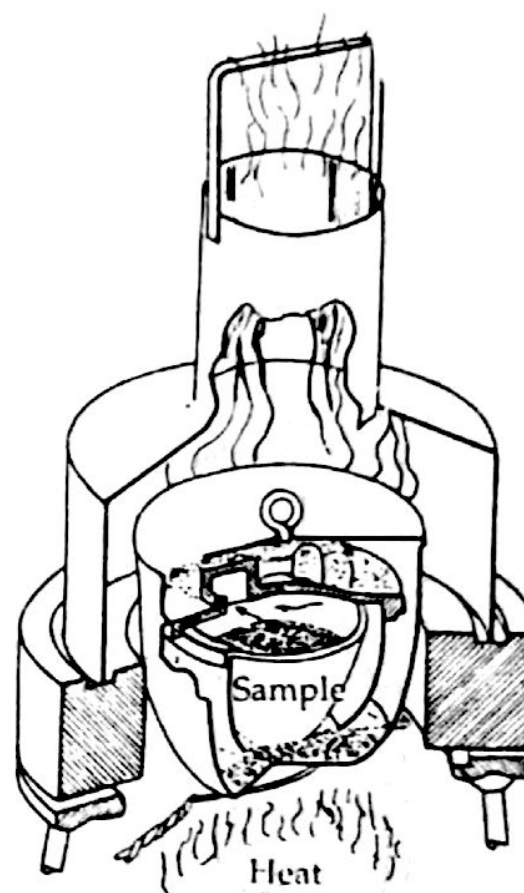


Fig. 20. (b) Cutaway view of couradson's apparatus.

**Procedure.** A weighed amount of sample is placed in a silica crucible (of about 65-85 mL capacity), which in turn is put into a skid more iron crucible having a close-fitting cover with a small horizontal opening. The crucibles are then placed into a larger third crucible also fitted with a cover fitted loosely to shaped iron hood. Heat is supplied from a Meker burner at certain prescribed rates till vapours of all volatile matter are burnt completely. After 30 minutes the silica crucible is removed, cooled in a desiccator, and weighed.

$$\% \text{ carbon residue} = \frac{\text{weight of residue in crucible}}{\text{Weight of original oil sample}} \times 100$$

(ii) *The Ramsbottom method.* This method is used with the more fluid products.

*Procedure.* A weighed sample is placed in a special glass bulb with a capillary opening. (The oil is injected into the bulb through the capillary inlet by means of a syringe). This glass bulb containing sample is inserted in one of the holes of an electrically heated small furnace (Ramsbottom apparatus) maintained at approximately 550°C. At this temperature, all volatile matter escapes the bulb capillary leaving a residue that undergoes cracking and possible coke formation. After the heating, the bulb is taken out, cooled in a desiccator and weighed.

$$\% \text{ carbon residue} = \frac{\text{weight of residue in bulb}}{\text{Weight of original oil sample}} \times 100$$

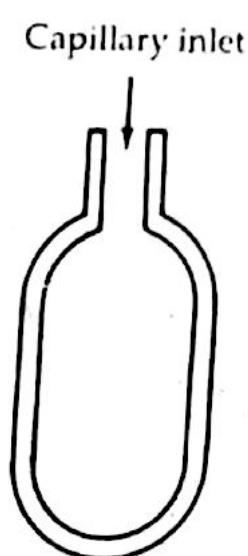


Fig. 21. (a) Glass bulb with a capillary opening.

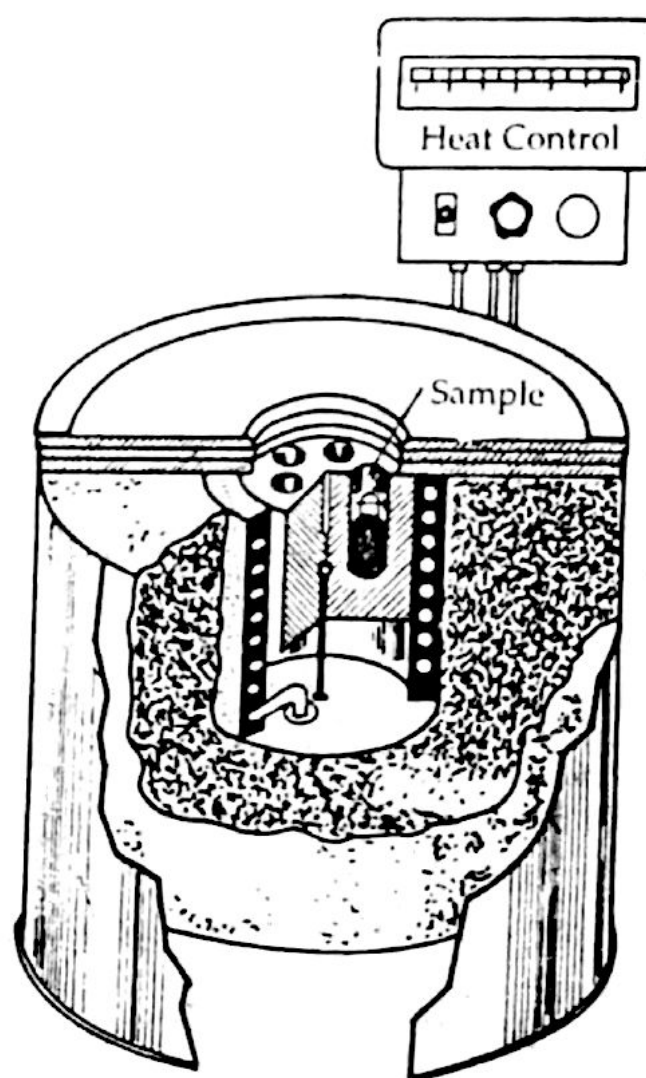


Fig. 21. (b) Cutaway view of Ramsbottom apparatus.

*Significance of carbon-residue tests.* Certain lubricating oils tend to deposit carbon in the combustion chambers of internal combustion engines, due to the carbonizing of the lubricating oil carried up past the piston rings into the combustion chambers. Incomplete combustion of fuel also results in carbon deposition. Excessive build-up of carbon deposits in the combustion chamber results in decreased volume of the charge at the end of the compression stroke giving increasing compression ratio which eventually leads to detonation. The data of carbon-residue tests are used in the evaluation of base crudes and feed stocks for the formulation of lubricants and fuels to be used in extreme temperature service.

**Exercises**

1. Write short notes on
 

(a) cloud and pour points	(b) Solid lubricants
(c) Greases	(d) Saponification and iodine value
(e) Viscosity and viscosity index	(f) Lubricants
(g) Lubricating action of greases	(h) Solid lubricants
(i) Synthetic lubricants	(j) Aniline point
(k) Boundary lubricants	
2. (a) How will you select a lubricant?  
 (b) Explain the classification and composition of lubricants.  
 (c) How is the viscosity of a lubricating oil determined in the laboratory?
3. (a) What is the significance of flash-point?  
 (b) How is viscosity-index calculated for unknown oil?  
 (c) Synthetic lubricants have added advantage over natural lubricants. Explain.
4. (a) What is meant by lubricant? Explain the mechanism of lubrication.  
 (b) Discuss the functions of lubricant.  
 (c) With the help of a neat diagram, explain the working of Redwood viscometer.
5. Describe flash-point determination by Pensky-Marten's method. What is the significance of the test?
6. (a) What type of lubrication is applied to delicate instrument? Explain its mechanism.  
 (b) Comment on the criteria for selection of lubricants for specific purposes.  
 (c) Fatty oils are no longer used as lubricants. Why?
7. What do you mean by consistency and drop-point of a grease sample?
8. Discuss the significance of
 

(a) Oiliness,	(b) Pour-point.
(c) Oxidation stability in the selection of liquid lubricants for practical purposes.	
9. Discuss extreme-pressure lubrication and additives to improve the lubricant properties.
10. (a) Write short note on structure of graphite and its use as a solid lubricant.  
 (b) Give a short account of fluid-film lubrication and boundary lubrication.

**R.G.P.V. Examination Questions**

1. (a) Define lubrication. Explain the mechanism of boundary lubrication.  
 (b) Explain the following properties of lubricants and give their significance :  
 (i) Aniline point.      (ii) Cloud point and pour point.      [Feb. 2005, 20 marks]
2. (a) Explain the following properties of lubricants and discuss their significance :  
 (i) Flash and fire points.      (ii) Cloud and pour points.  
 (iii) Saponification number.  
 (b) A lubricating oil has a S.U.V. of 58 sec at 210°F and 600 sec at 100°F. The high viscosity index standard (i.e., Pennsylvanian) oil has S.U.V. of 58 seconds at 210°F and 400 seconds at 100°F.  
 The low viscosity index standard (i.e., Gulf) oil has a S.U.V. of 58 seconds at 210°F and 800 sec at 100°F. Calculate the viscosity index of the oil.  

[Dec. 2003, 20 marks]

[Dec. 2003, 5 marks]
3. Write short note on solid lubricants.



4. (a) Explain the following properties of lubricants (any two) :  
 (i) Flash and fire points, (ii) Cloud and pour points,  
 (iii) Neutralization number, (iv) Aniline point.
- (b) An oil sample under test has a saybolt universal viscosity of 64 seconds at 210°F and 564 seconds at 100°F. The low viscosity standard (Gulf oil) possesses a saybolt viscosity of 64 seconds at 210°F and 774 seconds at 100°F. The high viscosity standard (Pennsylvanian oil) gave the saybolt viscosity values of 64 seconds at 210°F and 414 seconds at 100°F. Calculate the viscosity-index of the oil sample under test.
- (c) Discuss the mechanism of hydrodynamic lubrication. [Dec. 2000, 16 marks]
5. (a) How are lubricants classified ?  
 (b) What are the different mechanisms of lubrication ? Discuss boundary film lubrication.  
 (c) What are greases ? Mention their some specific uses. [Dec. 2001, 16 marks]
6. (a) Explain the following properties of lubricants and their significance : (i) carbon residue, (ii) aniline point.  
 (b) Write information note on synthetic lubricants.  
 (c) Match the following :
- |                           |                         |
|---------------------------|-------------------------|
| (I) Graphite              | (1) Calcium soap base   |
| (II) Antiwear additives   | (2) Exanol              |
| (III) Cup greases         | (3) Tricresyl phosphate |
| (IV) Polymeric thickeners | (4) Solid lubricant.    |
- [Ans. I-4 ; II-2 ; III-1 ; IV-3]
- (d) Discuss, in brief, lubrication, its mechanism and significance. Explain viscosity index of lubricating oil. [June 2001, 20 marks]
7. (a) Define and classify the term "lubricants" mention their important functions. Explain and discuss the significance of any two properties of lubricants.  
 (b) A good lubricant has  
 (A) Low freezing point (B) Low vapour pressure  
 (C) High boiling point (D) All of the above [June 2002, 2003, 20 marks]
8. (a) Write information notes on the following :  
 (i) Graphite (ii) Extreme pressure lubricant  
 (iii) Carbon residue test (iv) Viscosity and viscosity index.  
 (b) Comment on the following :  
 (i) An ideal lubricant should have low aniline point.  
 (ii) Flash point determination by closed cup apparatus gives lower value than that determined by an open cup apparatus.  
 (iii) Determination of power point of a lubricating oil has a greater significance. [June 2004, 20 marks]

### Solution of Selected Numericals

2. (b) Here  $L = 800s$ ,  $H = 400s$  and  $U = 600s$

So, viscosity-index of unknown lubricating oil

$$V.I. = \frac{L - U}{L - H} \times 100 = \frac{800 - 600}{800 - 400} \times 100 = \frac{200}{400} \times 100 = 50.$$

## Polymers

*"Next to acquiring good friends, the best acquisition is that of good books. Books, like friends should be few and well chosen. Like friends, too, we should return to them again and again for, like true friends, they will never fail us – never cease to instruct."*

### 1 INTRODUCTION

In this modern world, polymers are an integral part of everyone's life style. They have very diverse structures and applications ranging from domestic articles to sophisticated scientific and medical instruments. These materials have penetrated into almost all the applications like transport, agriculture, construction, education etc. These materials are used as Fibers, Rubbers, Plastics, Adhesives, Paints etc.

In fact, the very existence of life is virtually the formation, transformation and decomposition of biopolymers viz. carbohydrates, proteins and nucleic acids therefore, in view of their importance, a proper understanding of polymeric materials is very essential.

#### Characteristics of Polymers

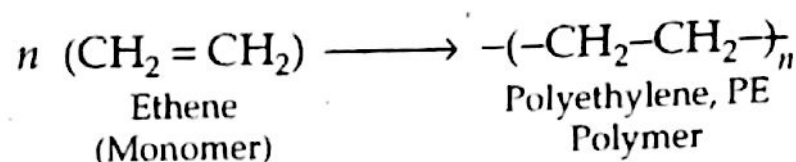
- Polymeric molecules are very big molecules. Their average molecular weights may approach  $10^5$  or more. That's why, they are also known as **macromolecules**. They are in fact, sub-microscopic particles.
- Polymers are semi-crystalline materials. It means they have both amorphous and crystalline regions. In fact, polymers have regions of crystallinity, called crystallites, embedded in amorphous regions. Crystallites provide strength and hardness and the amorphous regions provide flexibility to the polymeric material.
- The intermolecular forces in polymers can be Vander Waals' forces, dipole-dipole attractions or hydrogen bonding. These intermolecular forces are in addition to covalent bonds which connect the repeating units into a macromolecule.
- The chemical, electrical, optical, mechanical and thermal properties of polymers depend on (i) size and shape of polymers, and (ii) the presence or absence of characteristic intermolecular forces. These parameters not only determine the properties of the polymers, but also the performance of these materials in a given applications.
- Polymers show time-dependent properties. They show "creep" (their most significant mechanical characteristic).
- Polymers are combustible materials.
- Polymers have low densities and they show excellent resistance to corrosion.
- Generally, polymers are thermal and electrical insulators.
- Polymeric materials are tailor-made and are easily mouldable even into complex shapes with reproducible dimensions with a minimum of fabrication and finishing cost.

## 2 POLYMERS AND THEIR CLASSIFICATION

A **Polymer** is a long molecule formed by the joining together of thousands of small molecular units by chemical bonds. Due to their large size they are also sometimes called as *macromolecules*.

The chemical process leading to the formation of polymer is known as **Polymerisation** and the number of monomeric units contained in the polymer is known as **Degree of Polymerization**. Small molecules which combine with each other to form polymer molecules are known as **Monomers**.

For example :



where  $n$  is degree of polymerization, it can be  $10^4$  or more.

**Dependence of mechanical strength of commercial polymers on degree of polymerisation.**

In Fig. 1, mechanical strength of a commercial polymer is plotted against degree of polymerisation ( $\overline{DP}$ ). Different commercial polymers show similar trends but differing from one another in terms of the numerical value.

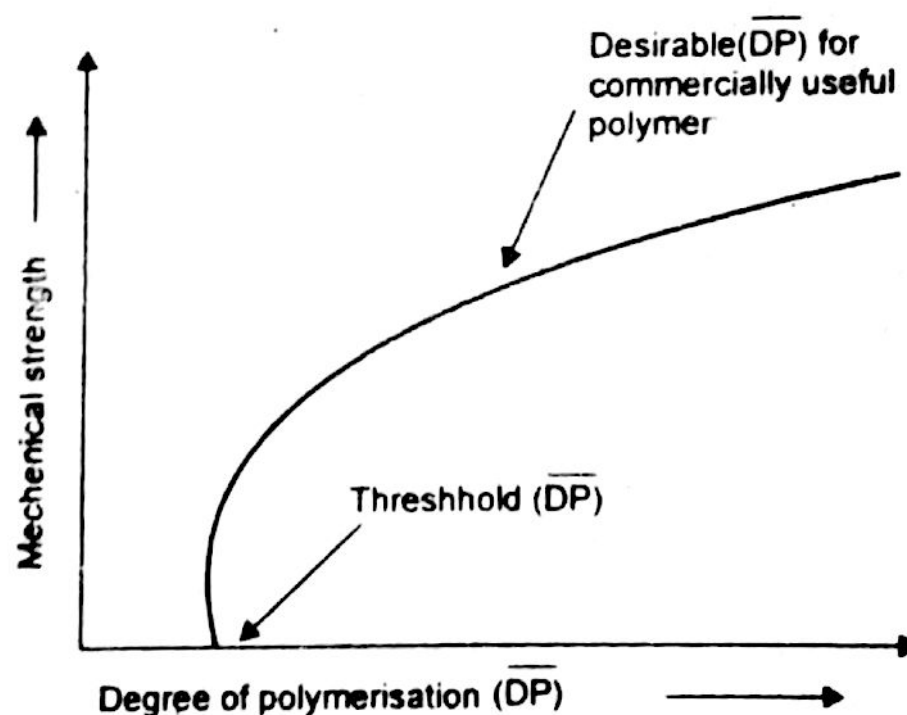


Fig. 1. Mechanical strength vs.  $\overline{DP}$  plot.

- Below threshold  $\overline{DP}$ , the polymer does not possess any strength and polymer exists either as liquid resin or friable powder. The threshold ( $\overline{DP}$ ) value is different for different polymers, for instance,

Polymer	Cellulose	Vinyl Polymers
Threshold ( $\overline{DP}$ )	60	~ 100

- In Fig. 1, the desirable  $\overline{DP}$  for commercial useful polymer is also marked. At this  $\overline{DP}$  value, the polymer attains more or less full strength. The optimum  $\overline{DP}$  values of some polymers are given below :

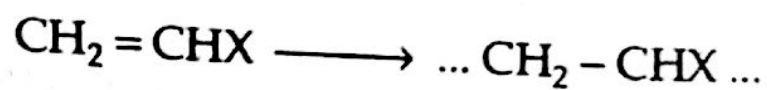
Polymer	Polyamides	Cellulose	Vinyl Polymers
Desirable ( $\overline{DP}$ )	150	250	400



## 2.1 Functionality

**Functionality** means the number of bonding sites in a monomer. The double bond in vinyl monomers ( $\text{CH}_2 = \text{CHX}$ ) can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination.

For example,



Thus, vinyl monomers can be considered as **bifunctional** because they have two reactive (or bonding) sites. For a substance to act as a monomer, it must have at least two reactive (or bonding) sites.

### Functionality and structures of polymers :

(i) When the functionality of monomer is two, linear or straight-chain polymer molecule is formed.

*Examples of Bifunctional monomers.* All vinyl monomers, Hexamethylene diamine, Adipic acid, Terephthalic acid, Ethylene glycol, Amino-acid, etc.

(ii) When the functionality of monomer is three, three-dimensional network polymer is formed.

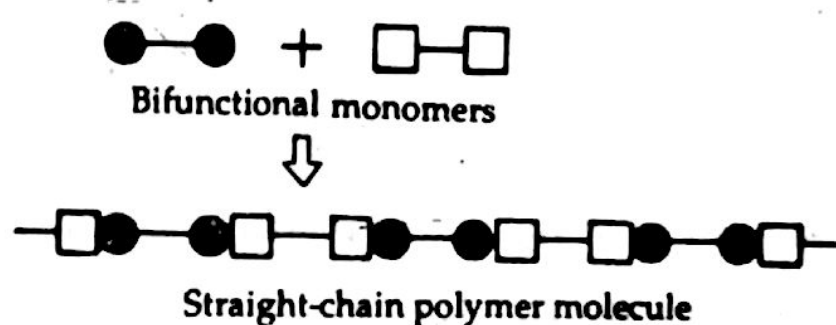
*Examples of Trifunctional monomers.* Phenol, Melamine, etc.

(iii) When a trifunctional monomer is mixed in small amounts with a bifunctional monomer, a branched chain polymer is formed.

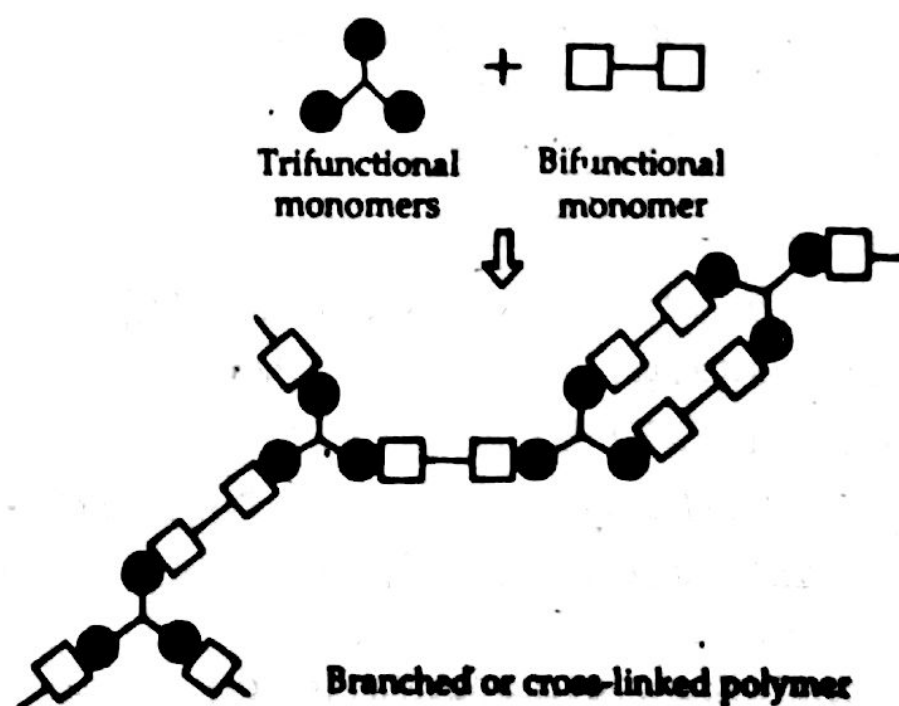
(iv) When a bifunctional monomer is mixed in small amounts with a trifunctional monomer, a three-dimensional network polymer is formed.

### Formation of linear and branched chains on the basis of functionality

#### I. Linear chain formation :



#### II. Branched chain (network polymer) formation :



**Example 1.** What is meant by functionality of a monomer.

**Solution.** Functionality means the number of bonding (or reactive) sites in a given molecule. The number of reactive functional groups (like  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NCO}$ ,  $-\text{SH}$ , etc.) per molecule of the compound defines its functionality.

**Example 2.** Why all simple organic compounds cannot act as monomer during polymerisation process?

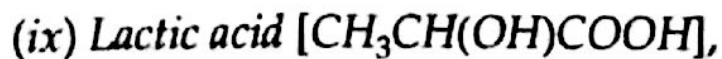
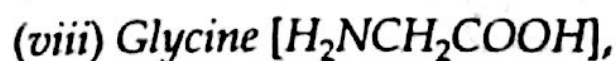
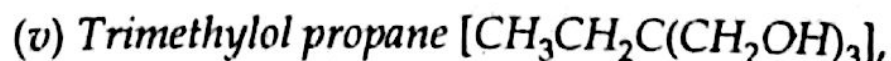
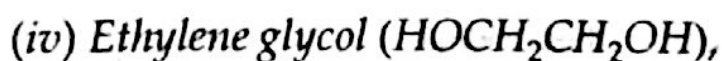
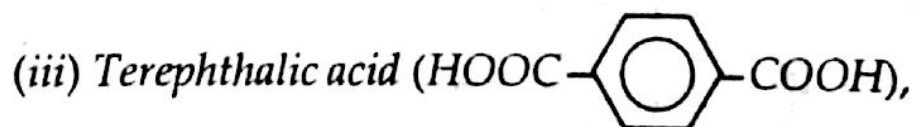
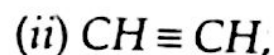
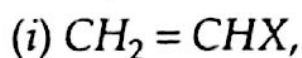
**Solution.** Because, for a substance to act as a monomer, it must be at least bifunctional. Thus, organic compounds like (i) Acetic acid ( $\text{CH}_3\text{COOH}$ ), (ii) Benzoic acid ( $\text{C}_6\text{H}_5-\text{COOH}$ ), (iii) Ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), (iv) Benzyl alcohol ( $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ), (v) Aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ), (vi) Methyl isocyanate ( $\text{CH}_3\text{NCO}$ ) etc. [which have only one functional group present per molecule] cannot act as monomer since they are monofunctional.

**Example 3.** Classify the following on the basis of their functionality : (i) Ethylene glycol, (ii) Vinyl chloride, (iii) Lactic acid.

**Solution.**

Compound	Chemical formula	No. of Double bonds per molecule	Number of functional gps. present per molecule		Functionality
			$-\text{OH}$	$-\text{COOH}$	
(i) Ethylene glycol	$\begin{array}{c} \text{CH}_2 - \text{OH} \\   \\ \text{CH}_2 - \text{OH} \end{array}$	—	2	—	Bifunctional
(ii) Vinyl chloride	$\text{CH}_2 = \text{CH} - \text{Cl}$	1	—	—	Bifunctional
(iii) Lactic acid	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}(\text{OH}) \\   \\ \text{COOH} \end{array}$	—	1	1	Bifunctional

**Example 4.** Classify the following into bifunctional, trifunctional and tetrafunctional organic compounds.



**Solution.** (a) Bifunctional organic compounds : (i), (iii), (iv), (vi), (vii), (viii), (ix).

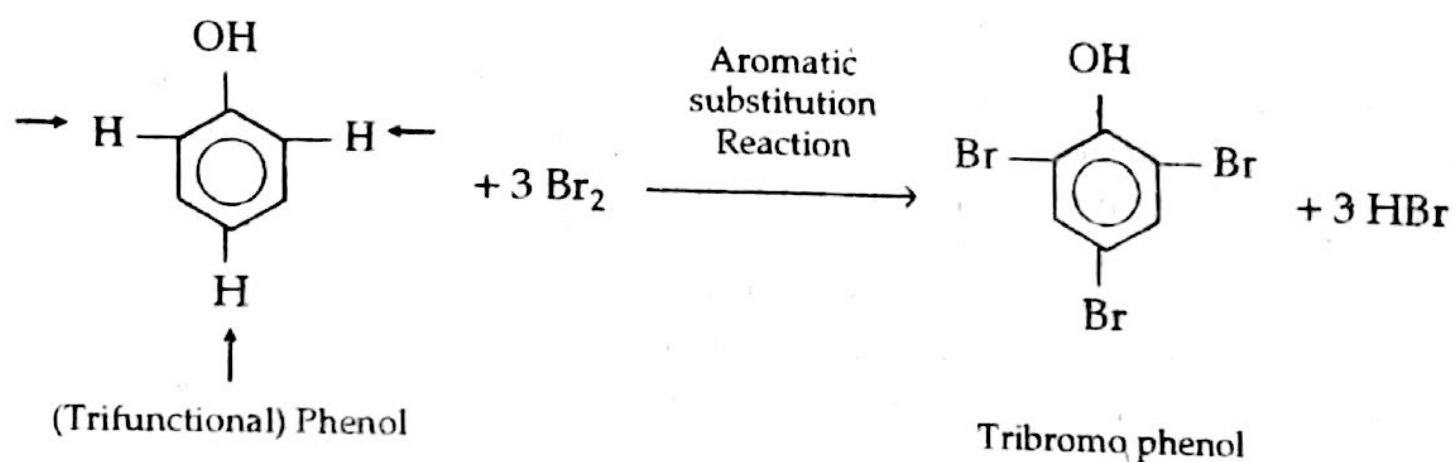
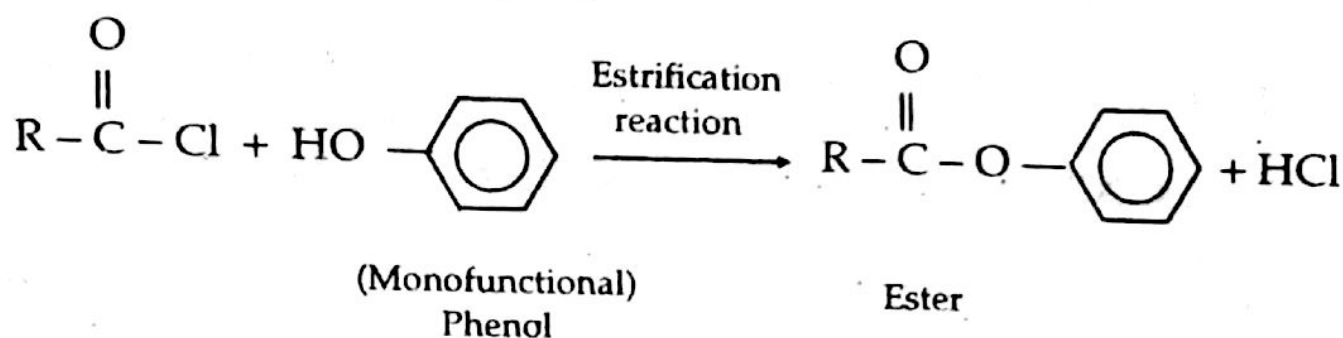
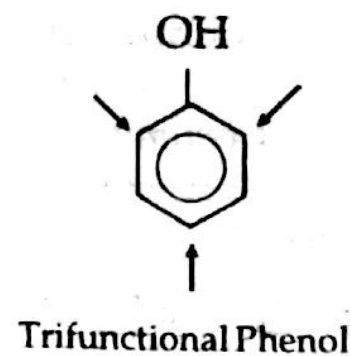
(b) Trifunctional organic compounds : (v),

(c) Tetrafunctional organic compounds : (ii), (x).

**Example 5.** Phenol can act as either monofunctional or trifunctional organic compound. Justify.

**Solution.** As phenol ( $C_6H_5OH$ ) possess one hydroxyl functional group (through which it undergoes esterification reaction) so it can act as monofunctional organic compound.

Furthermore, phenol has three easily replaceable hydrogen atoms (at ortho and para positions) for substitution reaction which imparts trifunctionality to phenol.



## 2.2 Polymer classification

### 2.2.1 Homo and Copolymers

**Homopolymers** are those polymers where the entire polymer chain is made of one single repeat unit.

Monomer	Repeat unit structure of polymer	Remarks
<b>Illustration</b> $n \text{ } \bullet \text{---}\bullet$		Homopolymer
<b>Examples</b> (i) $CH_2=CH_2$ Ethylene	$-[CH_2-CH_2]-_n$	Polyethylene homopolymer
(ii) $CH_2=CH$   Cl Vinylchloride		Polyvinylchloride homopolymer
(iii) $CH_2=CH$   OCOCH3 Vinylacetate		Polyvinyl acetate homopolymer



**Copolymers** are those polymers which have more than one type of repeat unit in the polymer backbone. The monomers from which the copolymer is made are called **comonomers**.

Comonomers	Repeat unit structure of copolymer	Remarks
<b>Illustration</b> $n \text{ (●—●)} + n \text{ (□—□)}$		Copolymer
<b>Examples</b> $\text{CH}_2=\underset{\text{Cl}}{\text{CH}} + \text{CH}_2=\underset{\text{OCOCH}_3}{\text{CH}}$ Vinyl chloride      Vinyl acetate		Poly (vinyl chloride - vinyl acetate) copolymer $\therefore$ Chain backbone is made of the two repeat units.

### Structure-Property Relationship

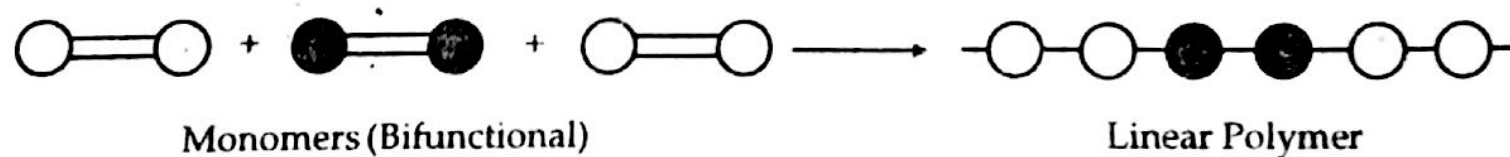
A linear homopolymer can easily crystallize but for comonomers the tendency for crystallization depends on whether the copolymer is alternate or random. For instance, a random copolymer is generally completely non-crystalline. This is because the random distribution of repeat units in the copolymer disturbs the structural regularity of the chain molecule and inhibit the tendency to crystallise. However, alternating copolymers, where the two repeat units are arranged in regular alternation, retain the structural regularity, and thus, can show a tendency to crystallise.

### 2.2.2 Linear, branched and cross-linked polymers

In **Linear Polymers**, each monomeric unit is linked with two other monomeric units on either side, forming a continuous straight chain. The monomeric units are added on to each other forming a long chain.

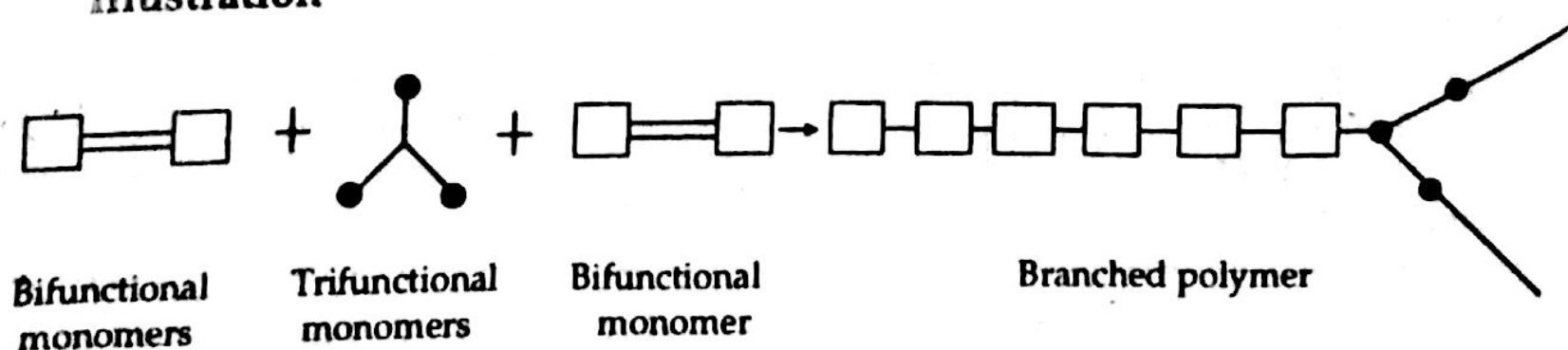
#### Illustration

**Example.** High density polythene is an example of linear polymer.



In **Branched polymers**, most of the monomeric units are linked with two other on either side, some monomeric units are linked with a third monomeric unit. Thus, apart from the growth of the polymer chain in a linear manner, some side growth also takes place from the main chain. Thus, structure of the branched polymer will be having mainly linear chains in it with a few short side chain or branches attached at random points. When a trifunctional monomer is mixed in small amounts with a bifunctional monomer, a branched chain polymer is formed.

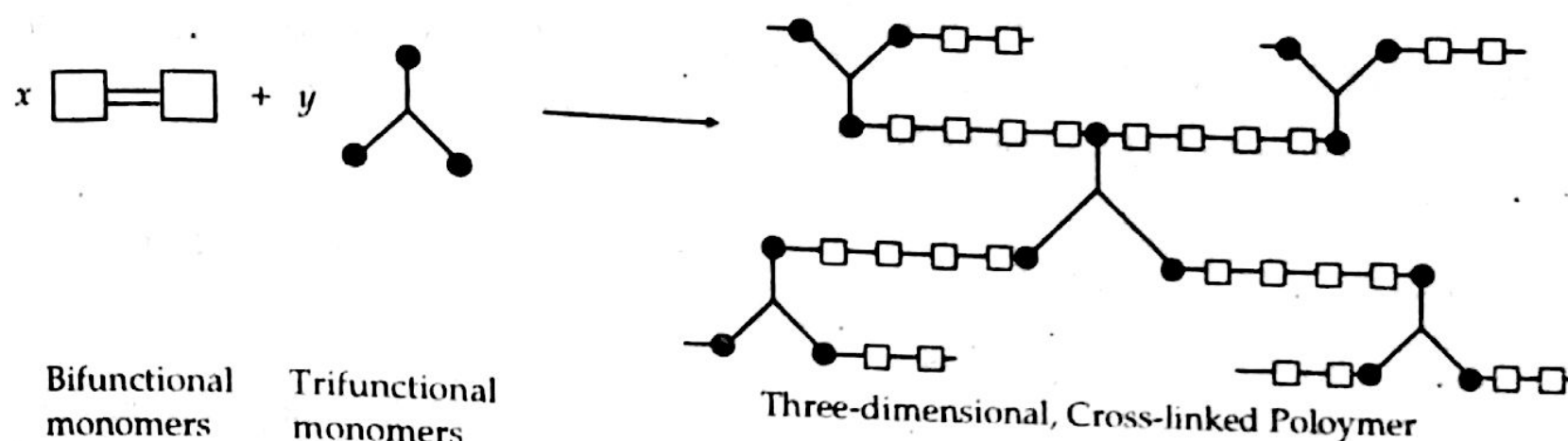
#### Illustration



**Example.** Low density polyethylene is an example of branched polymer.

In **cross-linked polymers**, a criss-crossed network of chain segments is there in all the three dimensions. When a bifunctional monomer is mixed in small amounts with trifunctional monomers, a three dimensional network polymer is formed which is known as cross-linked polymer.

**Illustration :**



**Examples.** Cross-linked polyethylene and all thermoset resins are examples of cross-linked polymers.

### Structure-Property Relationship

Linear polymer has highly regular configuration and is, therefore highly crystalline. The crystallinity reduces with extent of branching. Branched polymers find it more difficult to crystallise than linear polymers. This is because, branching imparts irregularity to the molecular structure and reduces the ability of the molecules to get themselves closely packed. The extent to which crystallinity is reduced depends on the pattern of branching.

Moreover, *Polymeric materials can be classified into several ways as described below :*

1. *Based on Structure/shape.* A polymer molecule may be Linear, Branched or cross-linked. Their structures & illustrative examples are given below :

Polymer	Structure	Examples
Linear		HDPE (High density polythene)
Branched		LDPE (Low density polythene)
Cross-linked		XLPE (Cross-linked polythene), Rubbers, Thermosets

2. *Based on Physical State.* A polymeric material can be Amorphous (e.g., LDPE, Rubbers etc.) or Semi-Crystalline (e.g., HDPE, Nylon, Polyesters).

3. Based on its behaviour when heated to Processing temperatures. Polymeric materials are broadly divided into two categories on this basis viz. Thermoplastics (e.g., PE, PP, PVC, Nylon, PET etc.) and thermosets (e.g., PF, UF, MF, epoxy etc.).

4. Based on end use. These include : Fibers (e.g., Polyester, Nylon etc.), Plastics (e.g., Thermoplastics and Thermosets), Elastomers (e.g., Rubber, Buna-S, Buna-N, Polyurethane etc.), Films (e.g., PP, LDPE, HDPE, PVC, PET etc.), Adhesives (e.g., PVA, epoxy resin etc.), Paints (e.g., epoxy etc.), Membranes (polyacetylene, polyaniline) etc.

5. Based on Tacticity (or Configuration)

Polymer	Structure	Model	Description
Isotactic		$\equiv$	Side groups are all on the same side
Syndiotactic		$\equiv$	Arrangement of side groups is in alternating fashion
Atactic		$\equiv$	Arrangement of side groups is at random around the main chain.

#### Structure-Property Relationship

- Isotactic, syndiotactic and atactic polymers have the same chemical structure but because of their different configurations they exhibit entirely different properties. For instance, isotactic and syndiotactic polymers are high melting and less soluble while atactic polymers are comparatively low melting and easily soluble. This is because stereo regular polymers (i.e., isotactic and syndiotactic) can easily crystallise whereas atactic ones are unable to do so.

6. Based on Origin. Polymers may be Natural (e.g., Carbohydrate, Proteins etc.) or Synthetic (e.g., Plastics, Rubbers, Fibers etc.) on this basis.

7. Based on Conductance. Polymers are mostly insulator (e.g., mostly all) but they can be conducting (e.g., Polyaniline, Polypyrrole etc.) also.

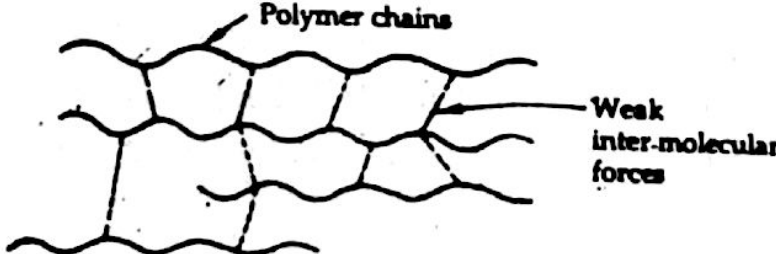
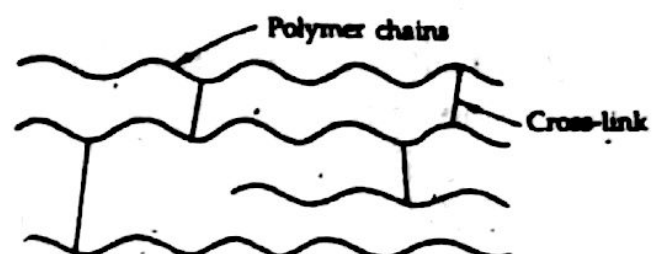
8. Based on Environment friendly nature. Polymeric materials can be durable (e.g., mostly all) or biodegradable (e.g., Starch based PE).



9. *Based on Type of monomers.* Polymers can be polar (e.g., PET, Nylon etc.) or non-polar (e.g., PE, PP etc.).

10. *Based on Number of monomers.* Polymers can be homopolymer (e.g., PE, PP, PVC etc.) or copolymer (e.g., styrene acrylonitrile copolymer, SAN etc.) when the number of monomers are one and two respectively.

*Differences between Thermoplastics and Thermosetting resins*

Thermoplastics	Thermosets
<p>1. They are formed either by addition or by condensation polymerisation reactions.</p> <p>2. They have either linear or branched structures.</p> <p>3. Adjacent polymer chains are held together by either van der Waals forces, or by dipole-dipole forces or by H-bonds.</p>  <p>4. They soften on heating and stiffen on cooling.</p> <p>5. Low molecular weight thermoplastics are soluble in their suitable solvents.</p> <p>6. They can be remoulded, re-shaped and re-used.</p> <p>7. They can be reclaimed from waste, i.e., they can be recycled.</p> <p>8. During moulding of thermoplastics, there is no change in their chemical composition.</p> <p>9. They are tough materials.</p> <p>10. Examples : PE, PP, PVC, PMMA, PS, PTFE, Nylons, Polyesters etc.</p>	<p>They are formed by condensation polymerisation reactions.</p> <p>They have three dimensional, cross-linked network structure.</p> <p>Adjacent polymer chains are held together by strong covalent bonds called cross-links.</p>  <p>They do not soften on heating.</p> <p>They are generally insoluble in any solvent.</p> <p>They can't be re-moulded and hence cannot be re-used.</p> <p>They cannot be re-claimed from waste. They cannot be recycled.</p> <p>They undergo chemical changes such as further polymerisation and cross-linking during moulding process.</p> <p>They are brittle materials.</p> <p>Examples : PF, UF, MF, Epoxy, XLPE etc.</p>

### 3 POLYMERS : AN OVERVIEW

Polymers contribute to national economy in terms of performance, reliability, cost-effectiveness and high added value.

*Advantages offered by Polymers in comparison with metals, wood, ceramics and other conventional materials :*

- (a) Polymers have low densities, this leads to production of light weight products, hence costs of transportation and general handling are low.
- (b) Polymers have low absolute strength and stiffness but their specific strength and specific stiffness values are favourable.
- (c) Polymers have excellent resistant to corrosion. They do not require any protective covering and the maintenance of exposed surface is easy and economical.
- (d) Polymers are usually thermal and electrical insulators.
- (e) Some polymers, especially rubbers, are inherently flexible. They also have excellent elasticity and damping qualities. (That's why they are used in springs and energy-absorbing mountings).
- (f) Polymeric materials are easily mouldable even into complex shapes with reproducible dimensions with a minimum of fabrication and finishing cost. This is because they require low processing temperatures, hence energy requirements are low.
- (g) Polymeric materials have the ability to take variety of colours, shades, etc. which do not fade easily since colouring is not usually restricted to the surface but is throughout the mass.
- (h) Polymeric materials are tailor-made. Depending on the need, they can be synthesized as (i) Transparent or opaque, (ii) Rigid (hard) or flexible (soft), (iii) Brittle or tough, (iv) Malleable or elastic and (v) Fibers (weavable), Elastomers (carvable) and Plastic (pourable).

*Drawbacks in Polymers compared with traditional materials :*

In comparison to traditional materials, polymeric materials have

- (a) Lower strength and stiffness, they easily get deformed under load,
- (b) Temperature limitations (hot or cold) in service, they have low heat resistance and at low temperatures, embrittlement occurs,
- (c) Time-dependent properties. They show "creep" (their most significant mechanical characteristic),
- (d) They are combustible but metals and ceramics are not.

*Where do we use these polymeric materials :*

- (a) We live in homes and move about in vehicles that are increasingly made of them, (like automobile wind screen, engine and body Parts, Floor Panels etc.) ;
- (b) We wear them, (by using Synthetic fabrics like Terylene etc.) ;
- (c) We sit and stand on them, (by making furniture from them) ;
- (d) We sleep between them, (by using foamed *matraces* and bed-sheets) ;
- (e) We eat and drink from them, (by using plastic crockery) ;
- (f) We see sights far away from us in time and space and we hear sound with their help (by making electrical appliances like TV and radio cabinets and telephone body etc.) ;

- (g) We turn knobs, pull switches and grasp handles made from them ;
- (h) Damaged organs (even entire heart) can be replaced or repaired with their help ;
- (i) We use them (in the form of ion-exchange resins) for the purification of water ;
- (j) By their use, blind people can be made to see and cripples to walk ;
- (k) In the form of coatings, they prevent rusting or decay of traditional materials ;
- (l) We employ them for electrical insulation for protecting ourselves against electric shock.
- (m) We also employ them for heat and sound insulation in refrigeration and air-conditioning (in buildings, auditoriums and theaters) ;
- (n) We also make overhead water tanks and pipes to convey water, gases, chemicals, oils etc., from them.

Industry wise, typical applications of polymers are summarized in Table 1.

**Table 1**

<i>End-Use Industry</i>	<i>Characteristics Required</i>	<i>Typical examples</i>	<i>Polymers</i>
Electrical Industry	Excellent insulation properties, flame retardant characteristics, toughness, durability	Wire and cable insulation Plugs, sockets,	PE, PVC PF
Building Industry	Economical, Durable, Aesthetics	Piping, Guttering and conduit, flooring, window frames	PVC
Packaging Industry	Light weight, Aesthetics, Protection	Films –For Food –For Textile Bottles –For cola drinks –For oils, squashes Containers for chemicals	(HDPE) (PP) (PET) (PVC) PVC
Auto-motive Industry	Light weight (Fuel economy), Safety, economy in manufacture, ease of maintenance, Aesthetics	Electrical equipments (batteries, flex, plug, switches) Under the bonnet applications (Radiator fans, drain plugs, petrol tubing and coolant water reservoirs) Bumpers, radiator grills etc.	“Speciality Plastics”
Leisure industry	Performance, Aesthetics, Durability	Photographic film Audio tapes, CD's Rackets (sports)	PET (PS) (PC) (glass or carbon fiber reinforced materials)



## 4 STRUCTURE AND TECHNOLOGICAL FUNCTION OF POLYMERS

### *Fibers, Elastomers and Plastics*

#### **Fibers**

They are thin, long, threadlike materials which have great tensile strength in the direction of the fibers. The strength of the fiber depends on the strength of the chemical bonds of the polymer chains.

The molecular shape of fiber forming material is linear. This linear shape permits side-by-side alignment. The long, thin and threadlike polymer molecules lie stretched out alongside each other, lined up in the fiber direction. The lining-up is brought about by stretching (*i.e.*, drawing) the polymer. Once lined up, the molecules do not return to random looped and coiled conformation. This is due to the strong intermolecular forces which maintain the alignment and prevent the "slipping" of one molecule past another. These intermolecular forces can be *vander Waals' forces* (which maintain the alignment of the stereoregular chains of isotactic polypropylene); *dipole-dipole attractions* (which maintain the alignment of chains of the Polyesters (Dacron, Terylene)) and Polyacrylonitrile ('Acrylic fibers', orlon); or *Hydrogen-bonding* (which maintain the alignment of the chains of polyamides (the nylons) and Polyurethanes (spandex, vycra)).

In addition, to be useful for clothing, it is preferable that the polymer has  $T_m > 200^\circ\text{C}$ , to allow ironing without damage, but lower than  $300^\circ\text{C}$ , to enable spinning from the melt. Also  $T_g$  must not be so high that ironing is ineffective. PET, nylon-66 and PAN all have  $T_g$  around  $100^\circ\text{C}$ , so that in a cloth the fibres will soften when ironed at about  $150^\circ\text{C}$ . This will remove creases or allow pleats to be made which will be retained on cooling. Subsequent washing is normally carried out at temperature too low to resoften the polymer significantly and so destroy the pleats. This "permanent" crease is a desirable feature of some clothing.

#### **Elastomers**

The elastomers possess the tendency to recover their original shape after they have been greatly deformed.

The elastomeric molecules are long and thin and flexible which become lined up when the material is stretched. But as soon as the stretching force is removed, the molecules return to their original random conformation. This is due to the absence of highly polar groups or sites for hydrogen bonding. Moreover, the extended chains do not fit together well enough for van der Waals forces to do the job. Hence, molecules in elastomers have *weak intermolecular forces*. For ready extension and recovery, the long chains of an elastomer must be connected to each other by occasional cross-links. These cross-links prevent the slipping of molecules past each other but at the same time, these occasional cross-links do not deprive the chains of their flexibility.

For example, Natural rubber (cis-1, 4-polyisoprene) has the structure.

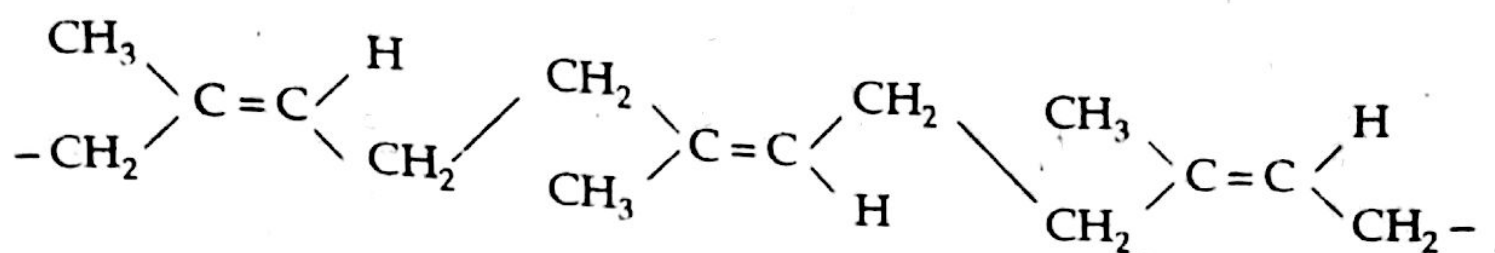


Fig. 2. Natural rubber

Due to the all cis-configurations about the double bonds, the chains do not fit together well. Hence there are only weak vander Waals' forces. Cross-linking between chains is done by heating with sulphur (vulcanization). This results in the formation of sulfur bridges between molecules.

### To Sum up

Long flexible chains, weak intermolecular forces and occasional cross-linking are the three essential structural requirements of an elastomer.

### Plastics

Broadly speaking, plastic can be of two general kinds : Thermoplastic and Thermosetting polymers.

*Thermoplastics* have either linear or branched structure. They can be amorphous or semicrystalline materials. Neighbouring polymeric chains are held together by weak van der Waals' forces or dipole-dipole forces or Hydrogen bonding. There are no cross-links. On Heating, they soften very readily but on cooling they stiffen again. That's why they can be remoulded, reshaped and reused. Hence, they can be reclaimed from wastes. These polymers are usually soluble in suitable solvents.

*Examples :* PE, PP, PVC, PMMA, Nylons, Polyesters, PS, PTFE, PVA, HIPS.

*Thermosetting polymers* have three dimensional, cross-linked networked structure. Neighbouring polymeric chains in thermosets are held together by cross-links (strong covalent bonds). Heating does not soften them, since softening would require breaking of covalent bonds.

In fact, they are made in two steps. First a low molecular weight, viscous liquid is obtained. Then heating is done in the presence of curing agent for the continuation of the polymerization coupled with the shaping of the product. Because, curing results in the formation of cross-linked network structure which cannot be remoulded, reused and reclaimed. These polymers are hard, strong, brittle and are generally insoluble in any solvent.

*Examples :* PF, UF, MF, vulcanized rubber, XLPE, EPOXY.

## 4.1 Structures and Applications

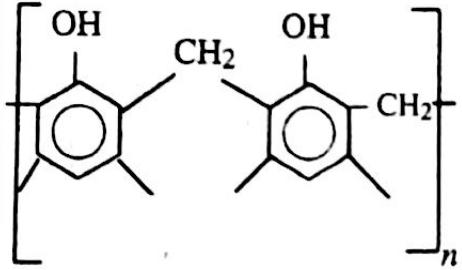
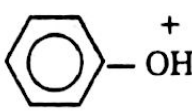
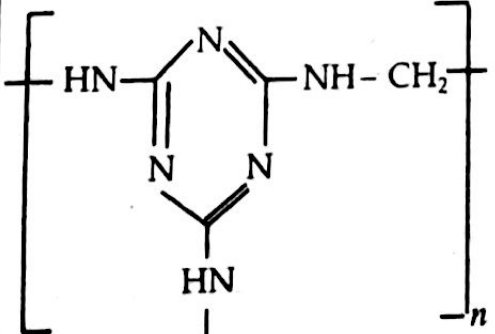
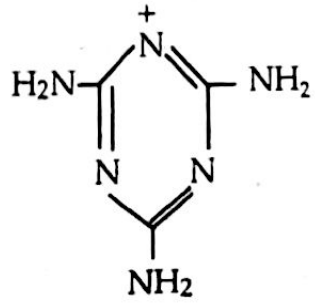
## I. STRUCTURES AND INDUSTRIAL APPLICATIONS OF IMPORTANT THERMOPLASTIC POLYMERS

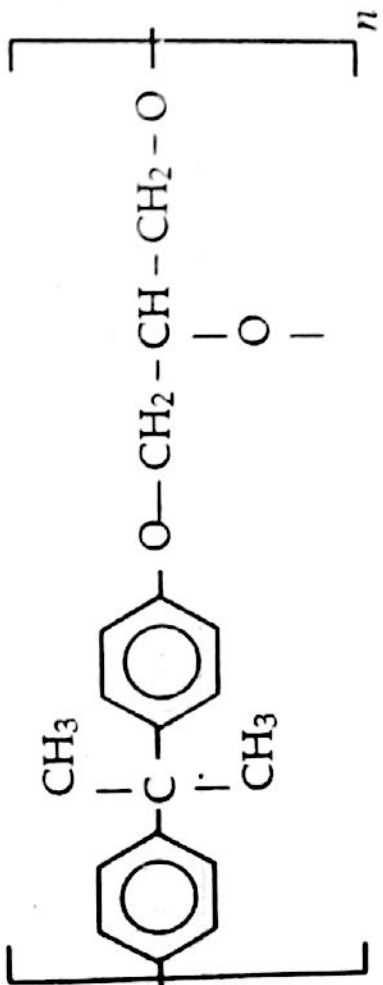

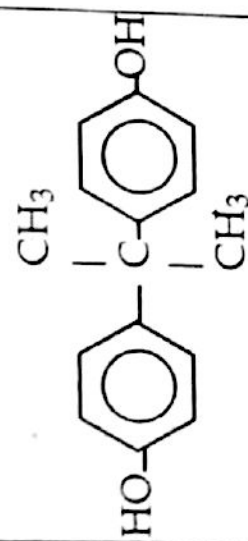
S.No.	Name of polymer	Structure of polymer	Monomer	Important Applications
1.	Polythene (PE)	$\text{-(CH}_2\text{-CH}_2\text{)}_n$	$\text{CH}_2=\text{CH}_2$ (Ethene)	<ul style="list-style-type: none"> <li>LDPE. As squeeze bottles for detergents, and wrapping material.</li> <li>HDPE. As anticorrosive packing material, insulator for wires and cables, household and laboratory wares [like toys, crates, closures, buckets, over head tanks, gas piping, milk bottles etc.]</li> </ul>
2.	Polypropylene (PP)	$\text{-(CH}_2\text{-CH(CH}_3\text{))}_n$	$\text{CH}_2=\text{CH(CH}_3\text{)}$ (Propene)	As Disposable syringes, Accelerator pedals, boxes, car-bumpers, films for wrapping confectionery items, chairs etc.
3.	Polystyrene (PS)	$\text{-(CH}_2\text{-CH(C}_6\text{H}_5\text{))}_n$	$\text{CH}_2=\text{CH(C}_6\text{H}_5\text{)}$ (Styrene)	<ul style="list-style-type: none"> <li>(In foamed form) as disposable drinking cups, cushioned packaging and thermal insulator ;</li> <li>In impact reinforced form as inner liners of refrigerators and radio/TV cabinets ; As raw material for preparation of synthetic ion exchange resins.</li> </ul>
4.	Poly vinyl chloride (PVC)	$\text{-(CH}_2\text{-CHCl)}_n$	$\text{CH}_2=\text{CHCl}$ (Vinyl chloride)	<ul style="list-style-type: none"> <li>Rigid PVC. For making window frames, doors, bottles, safety helmets, pipes etc.</li> <li>Plasticized PVC. For making kitchen upholstery, bathroom curtains, ladies hand bags and for insulation of domestic wires and cables.</li> </ul>
5.	Polymethylmethacrylate (PMMA)	$\text{-(CH}_2\text{-C(CH}_3\text{)(COOCH}_3\text{))}_n$	$\text{CH}_2=\text{C(CH}_3\text{)(COOCH}_3\text{)}$ (Methyl methacrylate)	<ul style="list-style-type: none"> <li>Medical Applications. Dentures, hard contact lenses, artificial eyes.</li> <li>Automotive Applications. Housing for rear lamps, light fittings, etc.</li> <li>As substitute of glass. As-plexiglass or Lucite for making TV screens, wind screens etc.</li> </ul>



S.No.	Name of polymer	Structure of polymer	Monomer	Important Applications
6.	Polytetrafluoroethylene (PTFE) or Teflon	$\text{---}[\text{CF}_2 - \text{CF}_2]_n\text{---}$	$\text{CF}_2 = \text{CF}_2$ (Tetrafluoroethylene)	As insulating materials for transformers, cables, wires, fittings, etc., As non-stick coatings for frying pans, As gaskets and seals, For stop-cock of burettes.
7.	Nylon-6	$\left[ \text{NH} - (\text{CH}_2)_5 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} \right]_n$	$\begin{array}{c} \text{H} \\   \\ \text{N} \\ \text{C} = \text{O} \\ (\text{CH}_2)_5 \\ \text{(Caprolactum)} \end{array}$	In making tyre cords, ropes, fibres and plastics.
8.	Nylon-66	$\left[ \overset{\text{O}}{\parallel} \text{C} - (\text{CH}_2)_4 - \overset{\text{O}}{\parallel} \text{C} - \text{NH} - (\text{CH}_2)_6 - \text{NH} \right]_n$	$\begin{array}{c} \text{HOOC} - (\text{CH}_2)_4 - \text{COOH} \\ \text{Adipic acid} \\ + \\ \text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2 \\ \text{Hexamethylene diamine} \end{array}$	As <b>fibers</b> : Automobile tyre cards, parachute ropes, threads and fibers for socks, undergarments, And carpets. As <b>plastics</b> : As metal substitute for gears and bearings, rollers, slides and door latches.
9.	Poly ethylene terephthalate (PET) or Terylene or Decron	$\left[ \overset{\text{O}}{\parallel} \text{C} - \text{C}_6\text{H}_4 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_2 - \text{CH}_2 - \text{O} \right]_n$	$\begin{array}{c} \text{HOOC} - \text{C}_6\text{H}_4 - \text{COOH} \\ \text{Terephthalic acid} \\ + \\ \text{HO} - \text{CH}_2 - \text{CH}_2 - \text{OH} \\ \text{(Ethylene glycol)} \end{array}$	As <b>plastics</b> . For making bottles for cola drinks, magnetic recording tapes, Housings for coffee machines, toasters etc. As <b>fibers</b> . For polyester shirts and garments ; tyre cords, tents etc.
10.	Poly acrylonitrile (orlon)	$\left[ \text{CH}_2 - \underset{\text{CN}}{\text{CH}} \right]_n$	$\begin{array}{c} \text{CH}_2 = \text{CH} \\   \\ \text{CN} \\ \text{(Acrylonitrile)} \end{array}$	For making synthetic fibers and synthetic wool.

## II. STRUCTURES AND INDUSTRIAL APPLICATIONS OF IMPORTANT THERMOSETTING POLYMERS

S.No.	Name of polymer	Structure of polymer	Monomer	Important applications
1.	Bakelite (PF resins)		<p>HCHO (Formaldehyde)</p> <p>             +            Phenol         </p>	<ul style="list-style-type: none"> <li>• Electrical fittings : Switches, plugs, heater handles, switch boards.</li> <li>• As abrasive wheels, sand paper and brake linings.</li> <li>• As moulded objects : Cabinets for radio/ TV, telephone and automobile parts.</li> <li>• As core binders in foundries (when mixed with sand).</li> <li>• For the manufacture of ion exchange resins for water softening.</li> </ul>
2.	Urea formaldehyde resin (UF resins)	<p> <math display="block">  \begin{array}{c}  -N-CH_2-N-CH_2-N-CH_2- \\    \quad   \quad   \\  O=C \quad O=C \quad C=O \\    \quad   \quad   \\  -N-CH_2-N-CH_2-N-CH_2-  \end{array}  </math> </p>	<p>HCHO (Formaldehyde)</p> <p>+</p> <p> <math display="block">  \begin{array}{c}  NH_2CONH_2 \\  \text{(Urea)}  \end{array}  </math> </p>	<ul style="list-style-type: none"> <li>• As moulded articles : Vacuum flask cups, bottle caps, buttons.</li> <li>• As adhesives : For plywood and laminating.</li> <li>• For the manufacture of cation exchange resins.</li> </ul>
3.	Melamine-formaldehyde resin (MF resins)		<p>HCHO Formaldehyde</p> <p>             +            (Melamine)         </p>	<ul style="list-style-type: none"> <li>• For making plastic crockery : Un-breakable cups and plates.</li> <li>• As tanning material for leather for strength improvement.</li> <li>• For manufacture of decorative laminates, And preparation of lacquers.</li> </ul>

S.No.	Name of polymer	Structure of polymer	Monomer	Important applications
4.	Epoxy resins		$\text{CH}_2 - \text{CH} - \text{CH} - \text{CH}_2\text{Cl}$  Epichlorohydrin  (Bisphenol-A)	As principal constituent of fibre-reinforced plastics (FRP's). For industrial floorings, foams. For electrical insulation. As Excellent structural adhesives.



### III. STRUCTURES AND INDUSTRIAL APPLICATIONS OF IMPORTANT ELASTOMERS

S.No.	Name of Polymer	Structure of Polymer	Monomer	Important Applications
1.	Styrene butadiene rubber (SBR or Buna-S)	$\left[ \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \right]_n$ <div style="text-align: center;"> <math>\text{C}_6\text{H}_5</math> </div>	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ <div style="text-align: center;">(Butadiene)</div> $+ \text{CH}_2 = \text{CH} - \text{C}_6\text{H}_5$ <div style="text-align: center;">(Styrene)</div>	In making footwear shoe soles and automobile tyres of lighter duty, for making hose, floor tiles, carpet backing.
2.	Nitrile rubber (Buna-N) (NBR or GR-A)	$\left[ \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \right]_n$ <div style="text-align: center;">CN</div>	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ <div style="text-align: center;">(Butadiene)</div> $+ \text{CH}_2 = \text{CH} - \text{CN}$	For manufacture of hoses and tank linings, In making oil seals, gasoline hoses, gaskets, fuel tanks etc.
3.	Neoprene or GR-M	$\left[ \text{CH}_2 - \text{C}(\text{Cl}) = \text{CH} - \text{CH}_2 \right]_n$	$\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$ <div style="text-align: center;">(Chloroprene)</div>	For making conveyor belts and printing rollers, For making tubings for carrying corrosive gases and oils, Its latex is used for the manufacture of gloves and coated fabrics, And it is used in oil resistant wire and cable coatings.
4.	Butyl rubber (GR-I)	$\left[ \text{CH}_2 - \text{C}(\text{CH}_3) = \text{CH} - \text{CH}_2 - \text{C}(\text{CH}_3)_2 - \text{CH}_2 \right]_n$	$\text{CH}_2 = \text{C}(\text{CH}_3)_2$ <div style="text-align: center;">Isobutene</div> $+ \text{CH}_2 = \text{C}(\text{CH}_3) - \text{CH} = \text{CH}_2$ <div style="text-align: center;">Isoprene</div>	For making inner tubes of tires, For wire and cable insulation, And for lining of tanks, hoses etc.

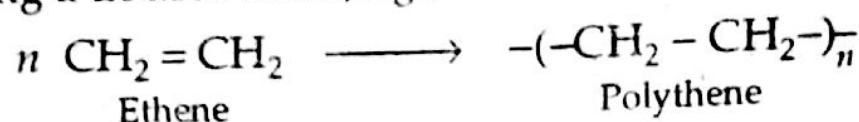
S.No.	Name of Polymer	Structure of Polymer	Monomer	Important Applications
5.	Polyurethane (PU) or Perlon-U	$\left[ \text{O} - (\text{CH}_2)_4 - \text{O} - \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \text{N} - (\text{CH}_2)_6 - \text{N} \begin{array}{c} \text{H} \\   \end{array} \text{C} \begin{array}{c} \text{O} \\ \parallel \end{array} \right]_n$	$\text{HO} - (\text{CH}_2)_4 - \text{OH}$ 1, 4-Butane-diol + $\text{OCN} - (\text{CH}_2)_6 - \text{NCO}$ 1-6-Hexamethylene diisocyanate	<ul style="list-style-type: none"> <li>• Flexible foam as upholstery material for furniture, pillows, mattresses, etc.</li> <li>• Rigid foam as core material for insulation in refrigerated appliances.</li> <li>• As fibers for making foundation garments and swim wear.</li> <li>• In encapsulation of integrated-circuit devices</li> <li>• In medical field, used in dental materials, artificial heart and skin.</li> </ul>

## 5 POLYMERIZATION

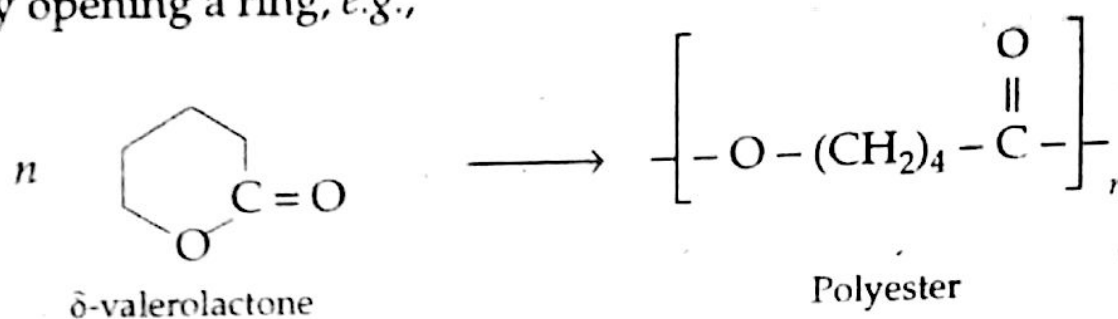
It is the process by which simple (monomer) molecules join together to form very large (polymer) molecules. Hence, the synthesis of large molecular weight polymers is termed as *Polymerization*.

There are three different ways for doing Polymerization :

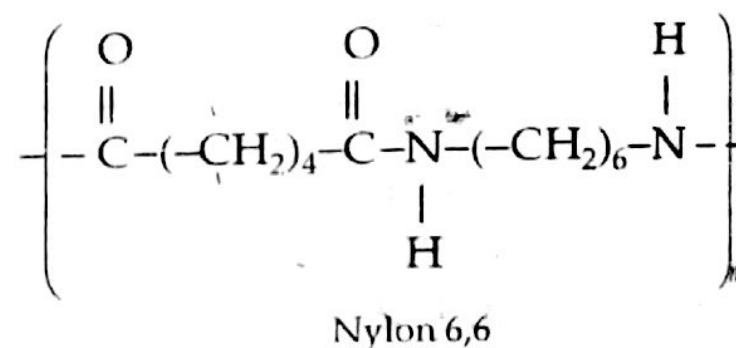
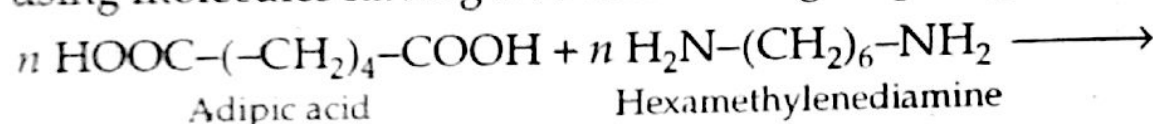
(a) By opening a double bond, e.g.,



(b) By opening a ring, e.g.,



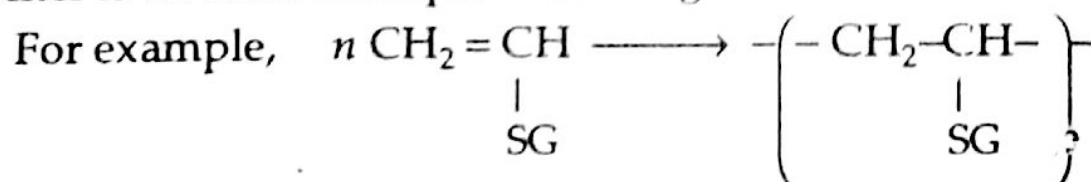
(c) By using molecules having two functional groups, e.g.,



These Polymerization reactions can be broadly classified into Addition and Condensation Polymerization. There are discussed below :

### 5.1 Addition Polymerization

Polymer synthesized by addition polymerization has the same empirical formula as that of monomer. No molecule is evolved during polymerization and the polymer is an exact multiple of the original monomeric molecule.



where

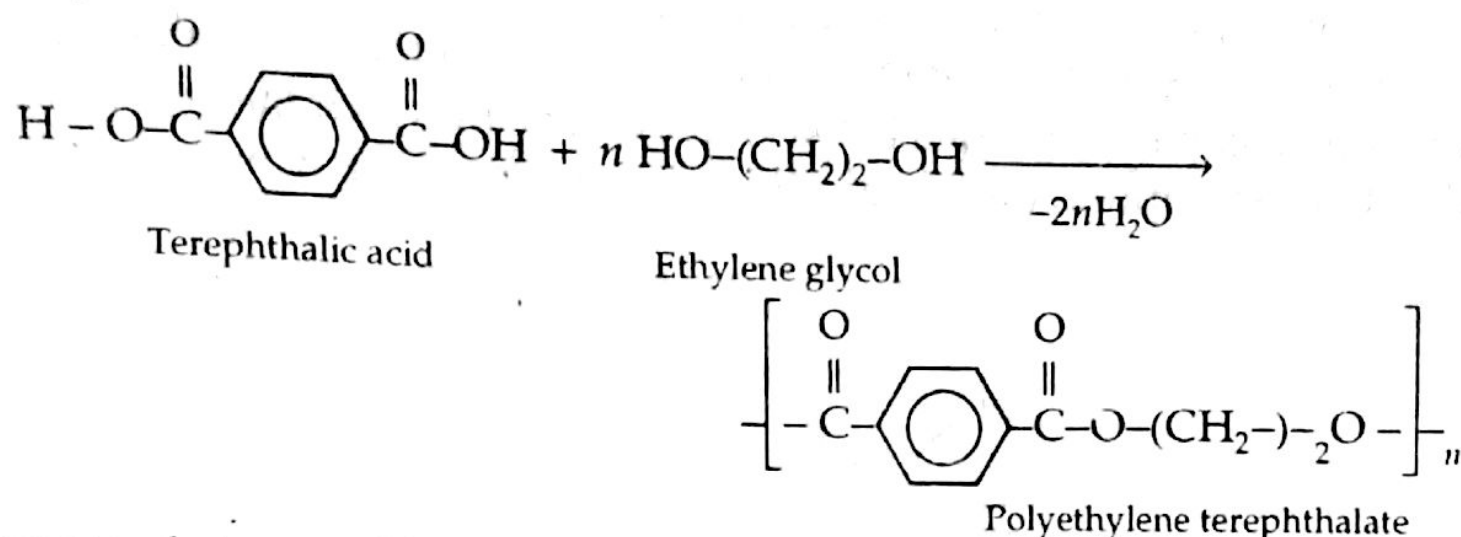
-SG (Substituent group)	-H	-CH <sub>3</sub>	-Cl	-C <sub>6</sub> H <sub>5</sub>
Polymer	Polyethene	Polypropylene	Polyvinyl Chloride	Polystyrene

### 5.2 Condensation Polymerization

It takes place by the condensation of two different bi- or poly functional monomers having functional groups which have affinity for each other. For example, -COOH and -OH or -COOH and -NH<sub>2</sub> carrying monomers undergo condensation polymerization.

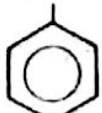



It always accompanies with the elimination of small molecules like  $H_2O$ ,  $HCl$  etc. For example :



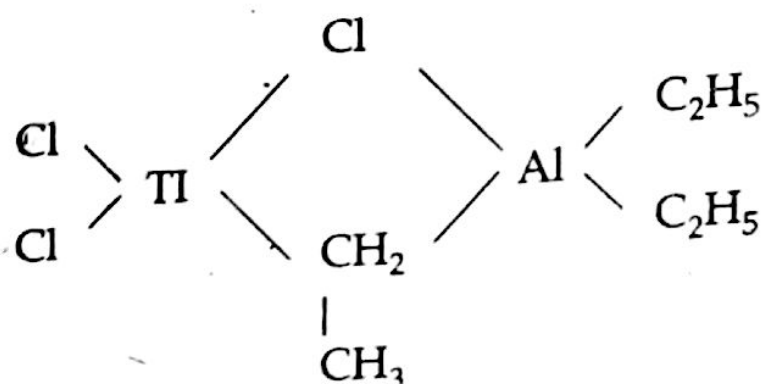
Differences between addition and condensation polymerization are summarized below in Table 2.

Table 2

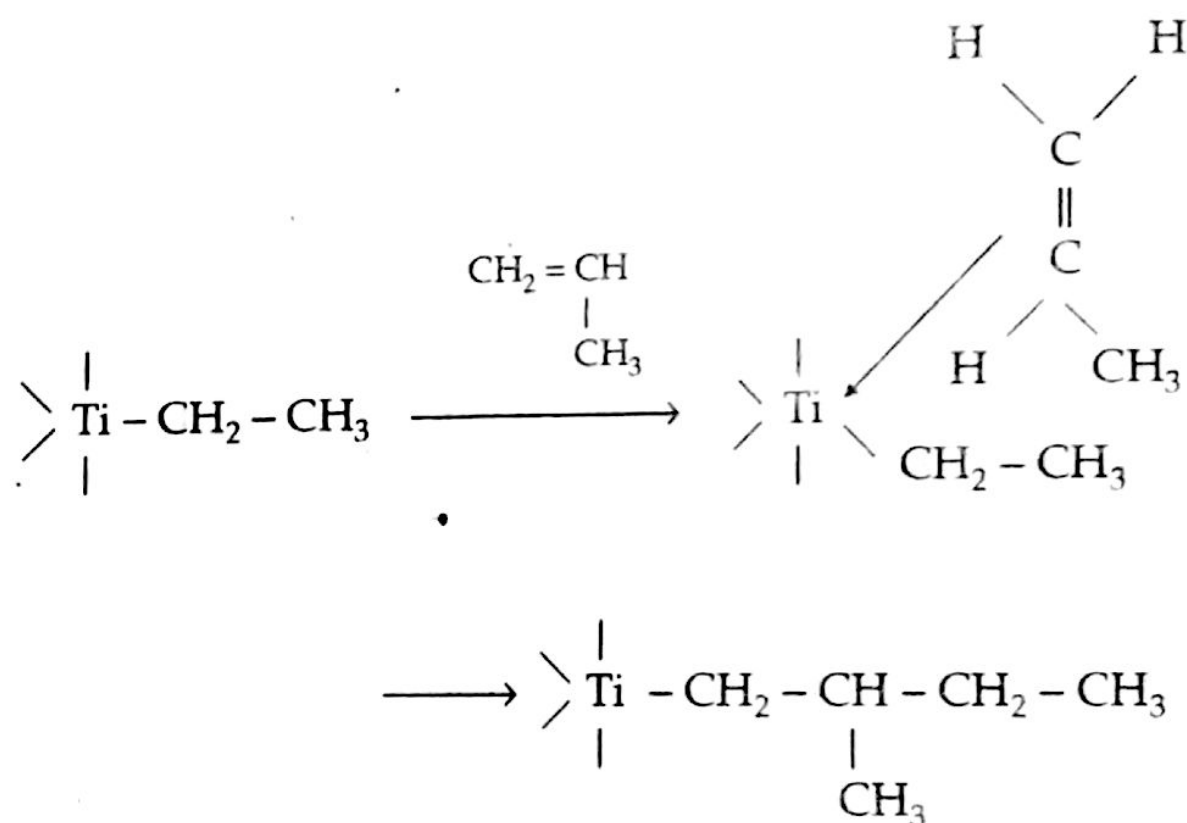
Addition Polymerization	Condensation Polymerization
<p>1. It requires the presence of double bond in the monomer.</p> <p>2. No by-product is formed.</p> <p>3. Homo-chain Polymer, generally a Thermoplastic is obtained.</p> <p>4. The growth of chain is at one active centre.</p> <p>5. <b>Examples of Addition Polymerizations</b></p> <p>(i) Polymerization of ethylene to form polyethylene (PE)</p> $n \text{CH}_2 = \text{CH}_2 \longrightarrow -[\text{CH}_2 - \text{CH}_2]_n$ <p style="text-align: center;">Ethylene                      Polyethylene</p> <p>(ii) Polymerization of vinyl chloride to form polyvinylchloride (PVC),</p> $n \text{CH}_2 = \text{CHCl} \longrightarrow -[\text{CH}_2 - \text{CHCl}]_n$ <p style="text-align: center;">Vinyl chloride                      Polyvinyl chloride</p> <p>(iii) Polymerization of styrene to form polystyrene (PS),</p> $n \text{CH}_2 = \text{CH} \longrightarrow -[\text{CH}_2 - \text{CH}]_n$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>Styrene</p> </div> <div style="text-align: center;">  <p>Polystyrene</p> </div> </div>	<p>It requires two reactive functional groups to be present at both ends of the monomer. There should be atleast two different bi- or poly functional monomers having functional groups with affinity for each other.</p> <p>Generally a by-product is formed.</p> <p>Hetero-chain Polymer either Thermoplastic or Thermoset can be obtained.</p> <p>The growth of chain occurs at minimum of two active centres.</p> <p><b>Examples of Condensation Polymerization</b></p> <p>Condensation polymerisation of hexamethylene diamine and adipic acid to form nylon 66 (polyamide)</p> $  \begin{array}{c}  n \text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2 \\  \text{Hexamethylene diamine} \\  + n \text{HOOC} - (\text{CH}_2)_4 - \text{COOH} \\  \text{Adipic acid} \\  \downarrow \\  -[\text{N} - (\text{CH}_2)_6 - \text{N} - \overset{\text{O}}{\parallel}{\text{C}} - (\text{CH}_2)_4 - \overset{\text{O}}{\parallel}{\text{C}}]_n \\  \begin{array}{ccccccc}    & &   & &    & &    \\  \text{H} & & \text{H} & & \text{O} & & \text{O}  \end{array} \\  \text{Nylon 66}  \end{array}  $ <p>(ii) Condensation polymerisation of caprolactum to form nylon-6.</p> <p>(iii) Condensation polymerisation of terephthalic acid and ethylene glycol to form polyethylene terephthalate.</p>

### 5.3 Coordination Addition Polymerization

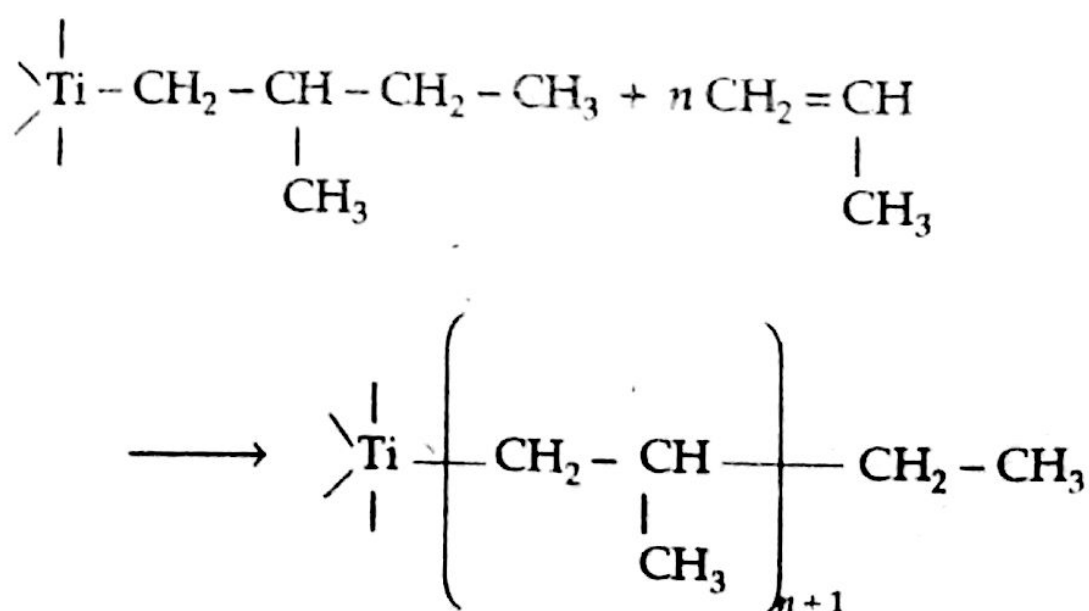
These polymerisation reactions are catalysed by Zeigler Natta catalysts formed between triethyl aluminium  $\text{Al}(\text{C}_2\text{H}_5)_3$  and titanium halide  $\text{TiCl}_3$ . A coordination complex is formed between these two, in which the ethyl group is coordinated to titanium, this is an active catalyst and its structure is shown below:



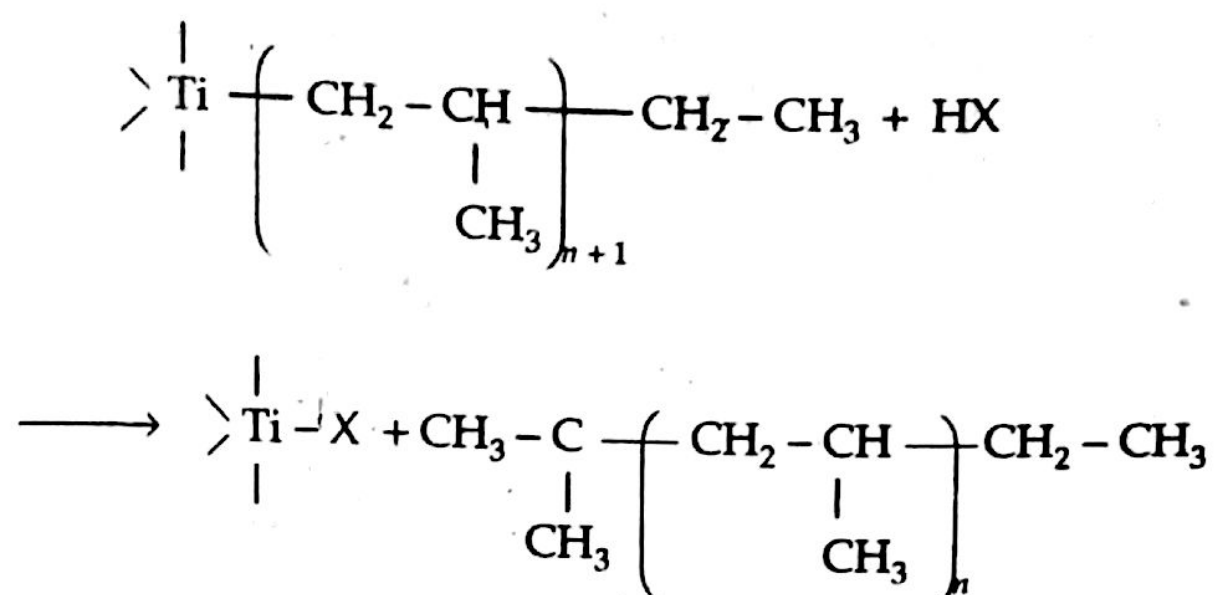
**Initiation :** In the initiation step,  $\pi$  - cloud of alkene overlaps with an empty orbital of titanium, then there is insertion of alkene molecule between the Ti - C bond.



**Propagation :** As intramolecular rearrangement again generates a vacant site on titanium, each time one monomer molecule can be added in the same fashion.



**Termination :** It can be done by the addition of molecules containing active hydrogen like HX.



#### *Significance of Coordination Addition Polymerization*

(1) It permits *stereochemical control*. For example, propylene when polymerized by this method preferentially forms isotactic polymer, but the conventional free radical polymerization results in atactic polypropylene. In isotactic PP, all the methyl groups are on the same side, this stereoregular arrangement results in higher melting point, hardness and superior properties. In contrast to this, in atactic PP, methyl groups attached to the polymer backbone are distributed at random. Hence, the resultant polymer is soft and elastic.

(2) *Linear polymer*, devoid of any branching, can be made. For instance, polyethylene made by Ziegler-Natta polymerisation is virtually free from any branching.

These unbranched PE molecules pack more efficiently, and this results in higher density and higher melting points of this polymer than the one obtained by free-radical addition polymerization.

(3) *Stereoselective synthesis* is also possible with coordination catalysts since they permit stereochemical control about the carbon-carbon double bond.

For example, isoprene can be polymerized by using Zeigler-Natta catalyst to cis-1, 4-polyisoprene, which is a material virtually identical with natural rubber.

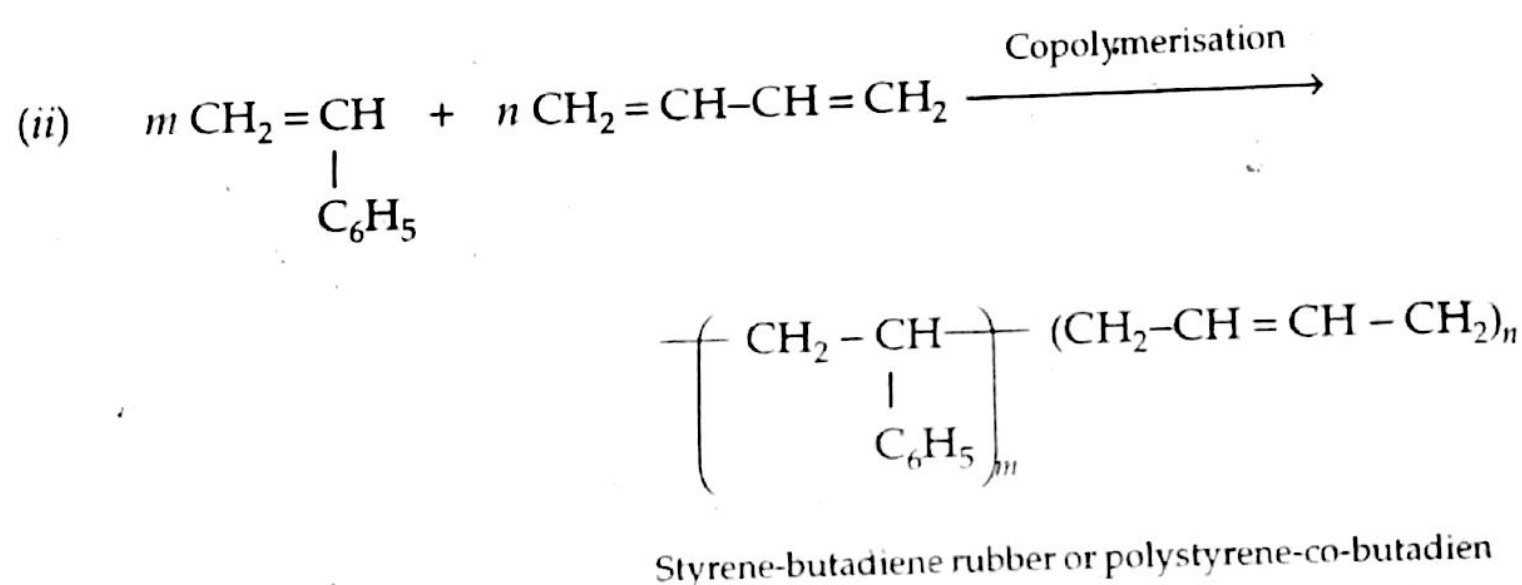
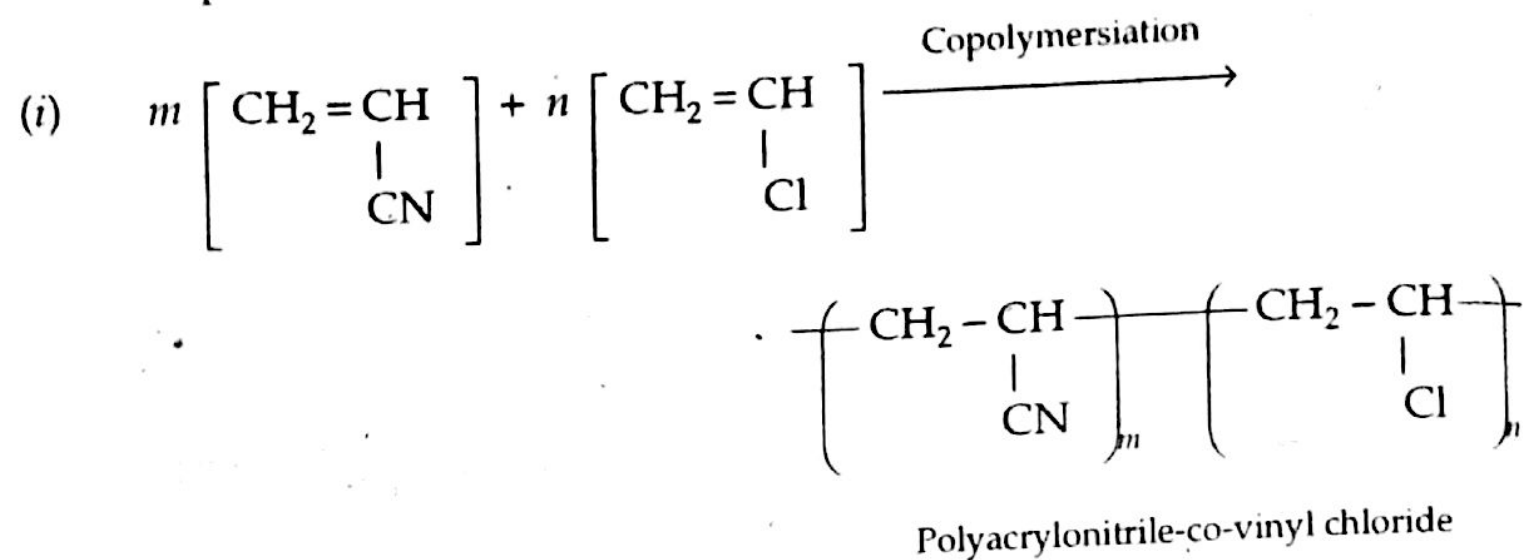
#### **5.4 Copolymerisation**

Copolymerisation has been used by nature in polypeptides which may contain as many as 20 different amino acids. Chemists are still far behind, but copolymers of two monomers, or terpolymers of three monomers, are now being widely produced.

Copolymerisation is a polymerisation of two or more monomeric species together.



For examples,



The resultant copolymers possess some advantageous properties which are required for end use. For example, styrene-butadiene rubber (SBR) has both rigidity and toughness. Moreover, it has good oil and petrol resistance.

The properties of copolymers depend on the type of monomers and how they link together in copolymers. Let us start with two monomers  $M_1$  and  $M_2$ . Then depending on their linking, the following four types of monomers are possible :

Copolymers	Structure	Description
Alternate	$-M_1 - M_2 - M_1 - M_2 - M_1 - M_2 -$	Monomers are arranged in regular alternate fashion.
Block	$\boxed{-M_1 - M_1 - M_1 -} - \boxed{M_2 - M_2 - M_2 -}$	A block of repeating unit of one kind of monomer is followed by block of another kind of monomer
Random	$-M_1 - M_2 - M_2 - M_1 - M_2 - M_1 - M_1 -$	Monomers are randomly distributed along the polymer chain.

Copolymers	Structure	Description
Graft		Have branched structures in which the monomer segments on the backbone and branches differ.

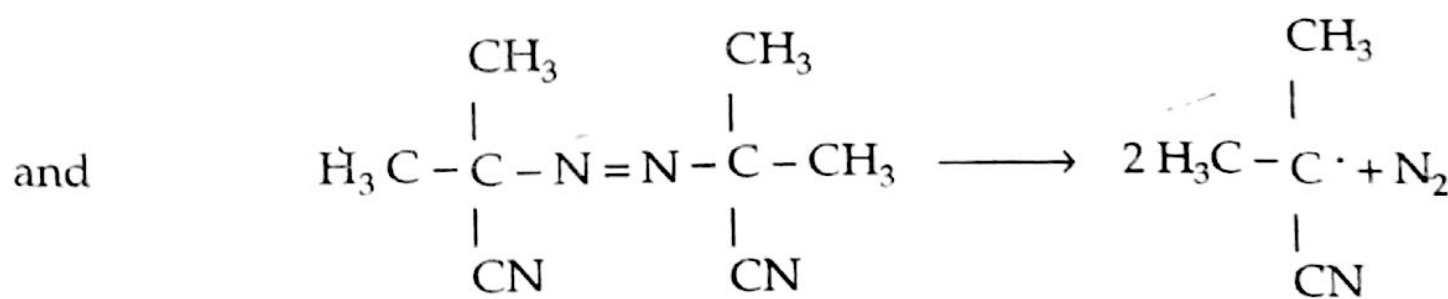
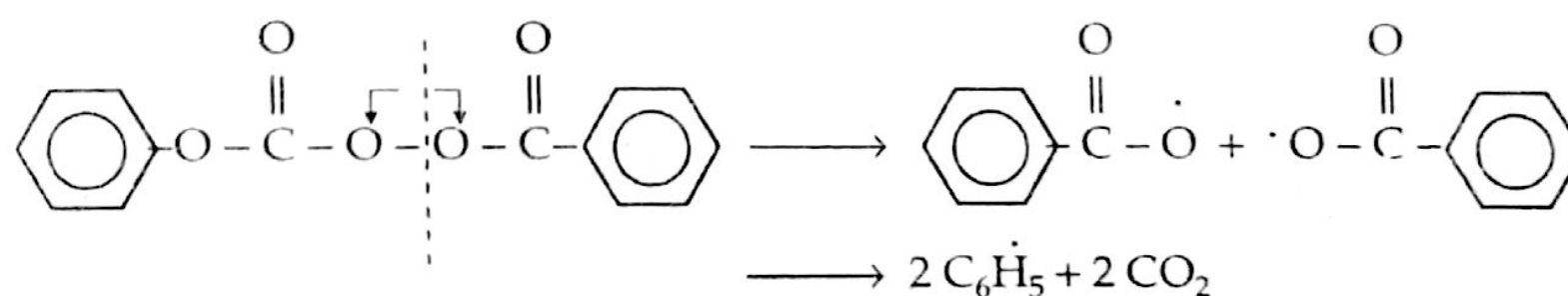
## 6 REACTION MECHANISM

### 1. Free-radical Polymerization

In free-radical polymerization, monomer is activated by its transformation into radical by the action of light (as in photochemically initiated), heat (as in thermally initiated), ionizing radiation such as  $\alpha$ ,  $\beta$  or  $\gamma$  radiations (as in radiation initiated) or by adding chemicals, known as initiators, (as in chemically initiated) free radical polymerization.

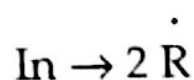
*Initiators* are the compounds which readily decompose into free radicals so that monomer molecules can interact with these free-radicals for their activation.

Examples of well known initiators are benzoyl peroxide and azobis iso butyronitrile (AIBN). They generate free radicals according to the following reactions :



Azobis iso butyronitrile (AIBN)

such reactions can be written in general as



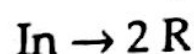
where In is a initiator molecule and R is free radical.

**Oxygen** is also known to initiate some free radical ethylene polymerization reactions. It occurs at higher temperatures by the thermal decomposition of the peroxides and hydroperoxides formed from the monomer.

The mechanism of free radical polymerization :

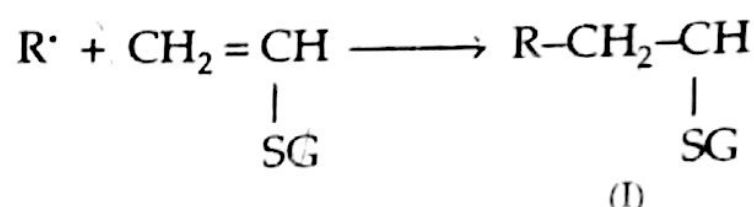
### Chain initiation

It involves two steps viz. decomposition of the initiator



and the addition of the first vinyl monomer  $\text{CH}_2 = \underset{\substack{| \\ \text{SG}}}{\text{CH}}$  molecule to the free

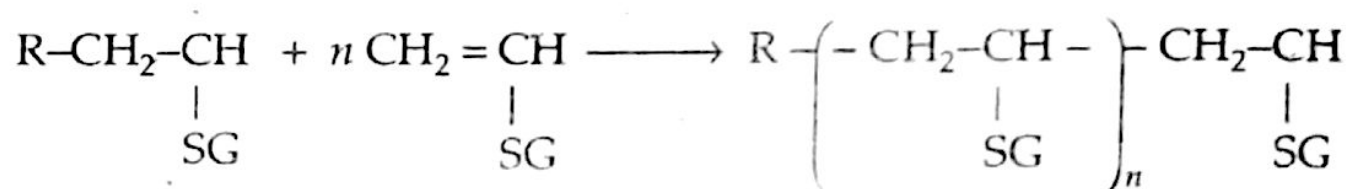
radical (R) and the formation of (I) as intermediate.



where SG is substituent group

### Chain propagation

It is accomplished by the addition of monomer molecules to (I) leading to the formation of macro-radicals. In general



The chain propagation steps determine

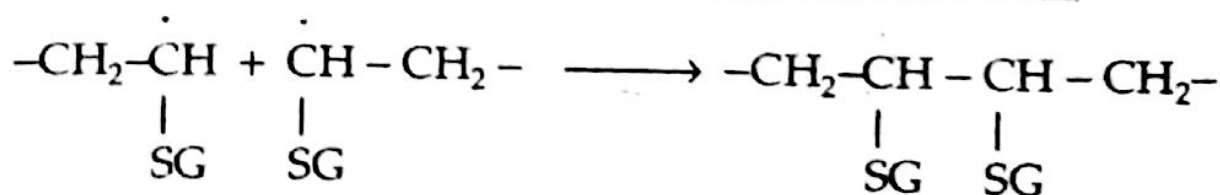
- (i) The rate of Polymerization,
- (ii) The molecular weight of the Polymer,
- (iii) The structure of the Polymer chain (the degree of branching due to chain transfer reactions) and
- (iv) The mode of monomer addition, as the reactive particle can attack an asymmetric vinyl monomer at either carbon atom of the double bond.

Generally, in a final polymer, monomer units are linked together in such a manner that they have substituents on alternate carbon atoms. This is known as *head-to-tail* or H-T or 1,3-placement of monomer units. This H-T placement is favored on both steric and resonance grounds.

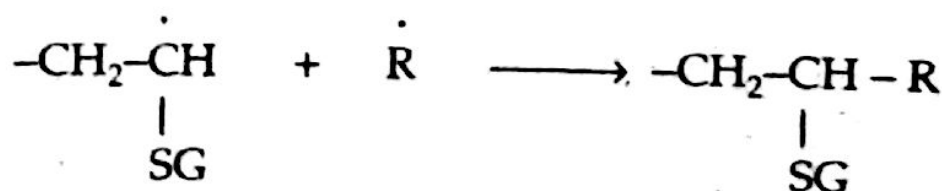
### Chain termination

The growing polymer chain can be terminated by

- (i) Recombination, which consists of combination of two radicals either



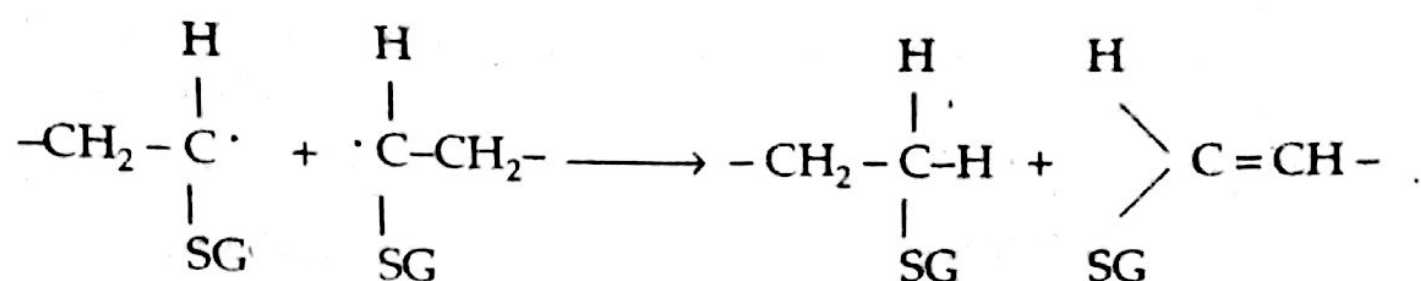
or



At  $T = 60^\circ\text{C}$ , "Polystyrene and acrylonitrile chains terminate mainly by recombination".



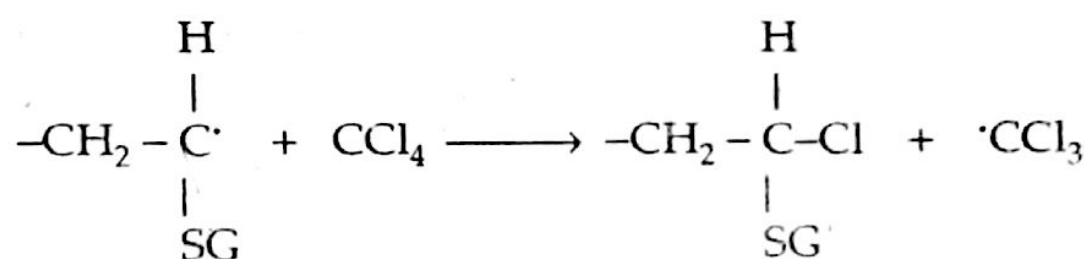
(ii) *Disproportionation* : It involves the transfer of a hydrogen atom of one macro-radical to another to form two macromolecules, one of them with a double bond at its end



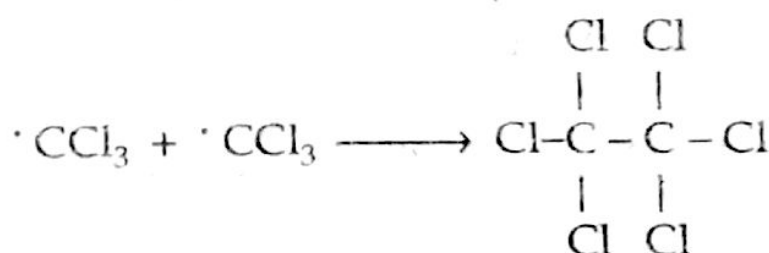
"At  $T \geq 60^\circ\text{C}$ , PMMA and vinyl acetate chains terminate mainly by disproportionation".

(iii) *Reaction with Polymerization inhibitors* : Growing polymer chain can also be terminated by its reaction with Polymerization inhibitors like hydroquinone and trinitrobenzene. Oxygen is also a powerful inhibitor as it reacts with radicals to form the relatively unreactive peroxy radical ( $\text{M}_n \cdot + \text{O}_2 \rightarrow \text{M}_n - \text{O} - \text{O} \cdot$ ) that reacts with itself or another propagating radical by coupling and disproportionation reactions to form inactive products (probably peroxides and hydroperoxides).

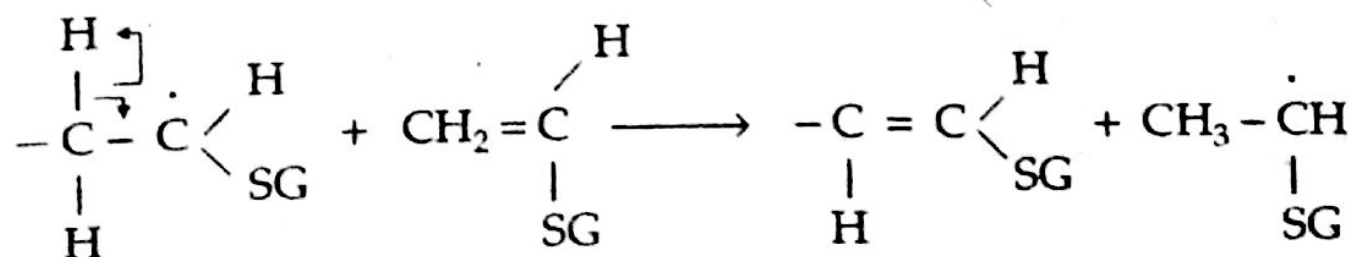
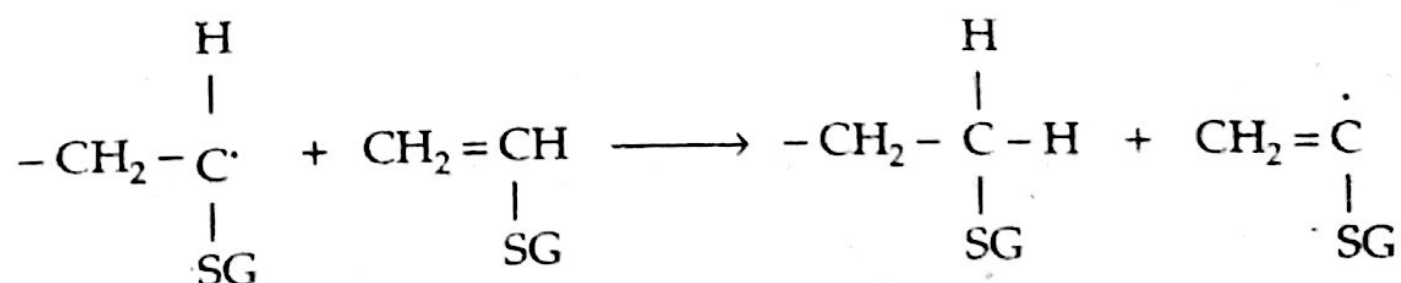
(iv) *Reaction with the solvent molecules (like carbon tetrachloride)*



Then

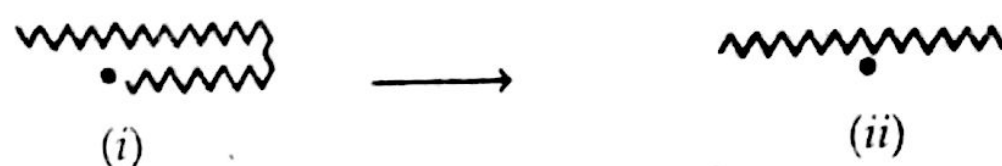


*Chain transfer reactions in free radical polymerization.* In these reactions, the original growing free radical chain is terminated by the reaction with the monomer molecule and a new chain is initiated.

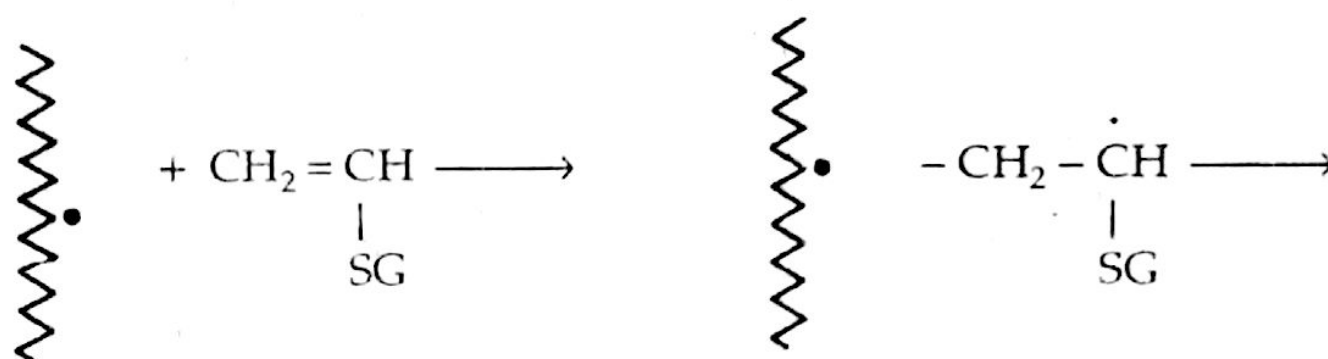


Hence, there will be no change in the overall rate of Polymerization but the average molecular weight of the Polymer will decrease.

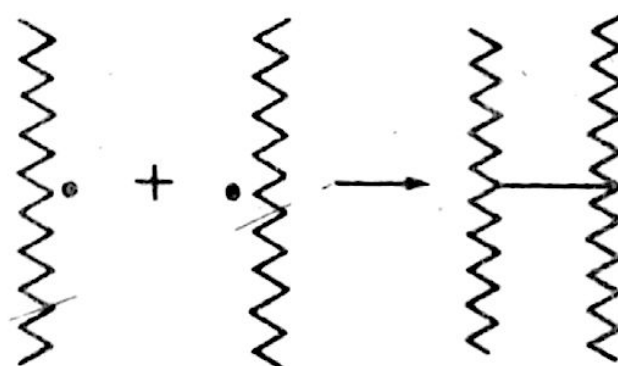
**Branching and cross-linking during the free-radical addition polymerization.** : Once a macroradical (i) is formed by the propagations of free-radical polymerisation reaction, back-biting can take place, leading to the abstraction of hydrogen atom (or any other univalent atom) from the middle of the chain. This leads to the transference of the active centres from the growing end of the polymer chain to the middle of the chain (ii)



Now, the propagation of reaction from middle centres will create branches, according to



There is also the possibility of reaction-between two molecules of type (ii), leading to the formation of cross-linkages.

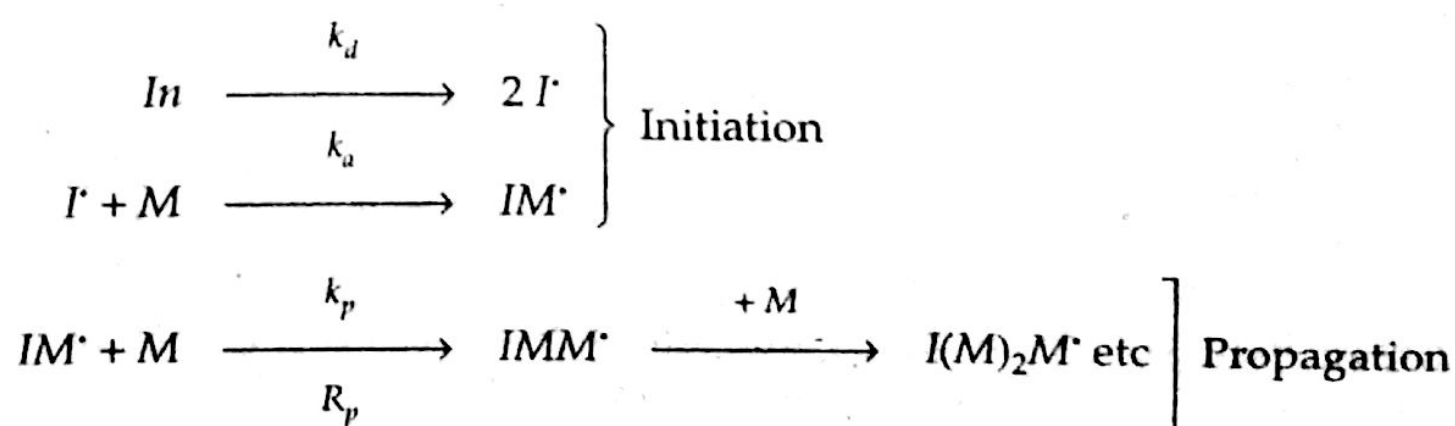


Monomers which can be polymerized by free radical addition polymerisation are :

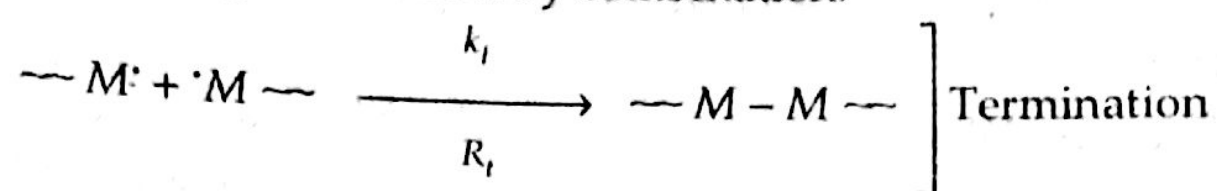
- (i) Ethylene and other vinyl derivatives like styrene, vinyl chloride etc.
- (ii) Acrylic acid derivatives like acrylates, methacrylates etc.
- (iii) Butadiene, isoprene and chloroprene etc.

### Kinetics of Free Radical Addition Polymerisation

The mechanism of a simple free radical initiated addition polymerization is rewritten below :



For simplicity, assuming termination by combination.



In the above mechanism,  $M$ ,  $In$ ,  $M^{\cdot}$  and  $I^{\cdot}$  indicate monomers, initiators and their radicals respectively, each initiator yielding two radicals.

Let  $f$  is the fraction of radicals which initiate chains, i.e., the initiator efficiency, and  $[In]$  is the concentration of initiator.

As  $k_d \ll k_a$

So, decomposition of  $In$  is rate determining step for initiation. Thus, the rate of initiation,  $R_i$  is given by

$$R_i = 2fk_d [In] \quad \dots(1)$$

The rate of propagation  $R_p$  is governed by the concentration of growing chains  $[M^{\cdot}]$  and of monomers  $[M]$ . This is also, in effect, the rate of monomer consumption so  $R_p$  also becomes the overall rate of polymerization

$$R_p = k_p [M] [\sim M^{\cdot}] \quad \dots(2)$$

The termination rate in mutual termination is determined by the concentration of growing radicals. This reaction is of second order as two radicals are involved in each termination :

$$R_t = k_t [\sim M^{\cdot}]^2 \quad \dots(3)$$

It is found in practice that the concentration of radicals quickly reaches a constant value and the reaction takes place in the steady state. This is known as *steady-state approximation* and is used for finding  $[\sim M^{\cdot}]$ .

Thus, the rate of radical formation ( $R_i$ ) becomes equal to the rate of radical disappearance, ( $R_t$ ).

$$\text{i.e.,} \quad [R_i] = [R_t] \quad \dots(4)$$

From equations (1) and (3), the above equation becomes

$$\begin{aligned} 2fk_d [In] &= k_t [\sim M^{\cdot}]^2 \\ \Rightarrow [\sim M^{\cdot}] &= \sqrt{2f \frac{k_d}{k_t} [In]} \quad \dots(5) \end{aligned}$$

This value of  $[M^{\cdot}]$  is then substituted in equation (2), we get

$$\begin{aligned} R_p &= k_p [M] [\sim M^{\cdot}] \\ &= k_p [M] \sqrt{2f \frac{k_d}{k_t} [In]} \\ R_p &= \left( 2f \frac{k_d}{k_t} \right)^{1/2} k_p [M] [In]^{1/2} \quad \dots(6) \end{aligned}$$



Equation (6) indicates that the  $R_p \propto \sqrt{[In]}$ , this is also found to be experimentally true.

Equation (6) also indicates that the  $R_p \propto [M]$ . But experimentally some deviations w.r.t.  $[M]$  are found. These deviations may in some cases be attributed to the dependency of  $f$  on  $[M]$  particularly at low efficiencies and in solution polymerizations, certain solvents may also affect the  $R_p \propto [M]$ .

The *average kinetic chain length* ( $r$ ). It is defined as the number of monomer units consumed per active centre formed.

$$r = \frac{R_p}{R_i} \text{ (or } \frac{R_p}{R_t} \text{)} \quad \dots(7)$$

From equations (1) and (6), the above equation becomes

$$r = \frac{(2fk_d/k_t)^{1/2} k_p [M] [In]^{1/2}}{2fk_d [In]}$$

$$r = \frac{k_p}{(2fk_d k_t)^{1/2}} \frac{[M]}{[In]^{1/2}} \quad \dots(8)$$

The *number average degree of polymerization* ( $\overline{DP}_n$ ). It is defined as the average number of monomer units per polymer chain.

Thus,  $\overline{DP}_n = r$  (if termination is by disproportionation)  
and  $\overline{DP}_n = 2r$  (if termination is by combination).

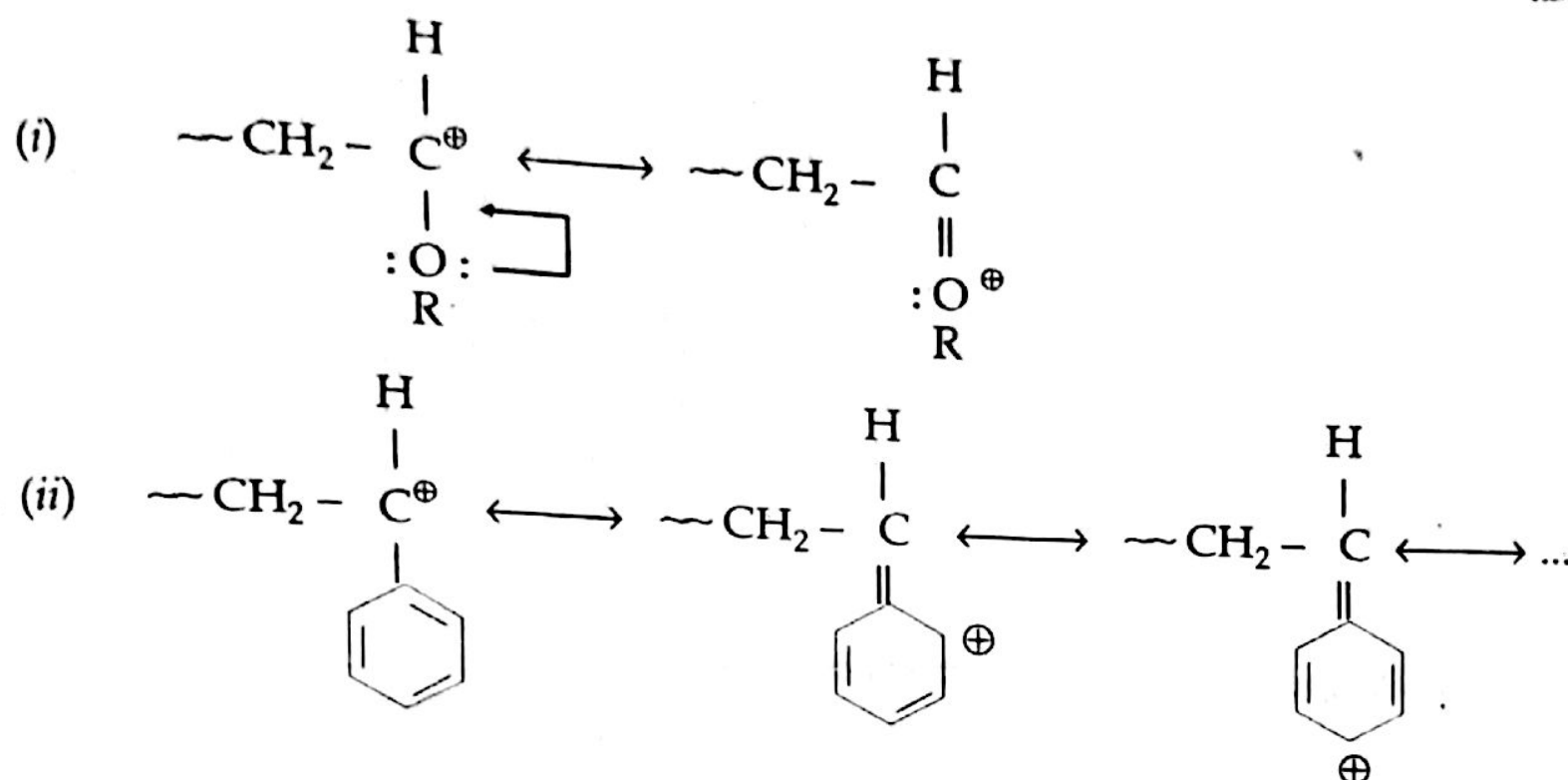
Thus, we can conclude from above relationships and equation (6), that while an increase in  $[In]$  increases the polymerization rate,  $R_p$ ; it decreases the  $r$ , or  $\overline{DP}_n$  or molecular weight.

## 2. Ionic Polymerisation

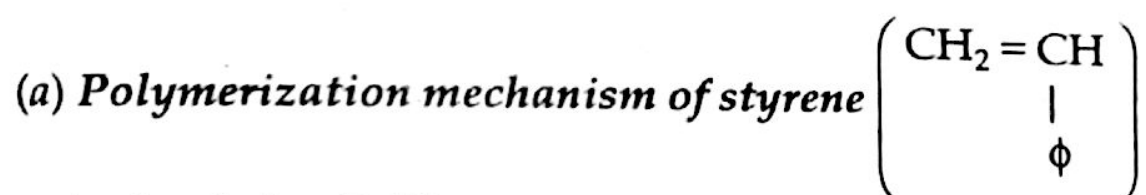
These are dependent on formation and propagation of ionic species. Relatively low or moderate temperatures are also needed to suppress termination, transfer, and other chain-breaking reactions which destroy propagating centers.

**(A) Cationic Polymerisation.** Monomers with electron releasing substituents (such as  $-OCH_3$ ,  $-OC_2H_5$  and  $-C_6H_5$ , etc.) undergo cationic polymerization in the presence of Lewis acids and Friedel Craft catalysts (like  $AlCl_3$ ,  $BF_3$ ,  $SnCl_4$  etc.). They add on to the monomer forming a carbonium ion. An essential feature of cationic addition polymerisation is that it takes place at very high rates, even at very low temperatures. Monomers like  $\alpha$ -methylstyrene, and isobutylene are preferably polymerized by this method as they do not polymerise well by other methods.

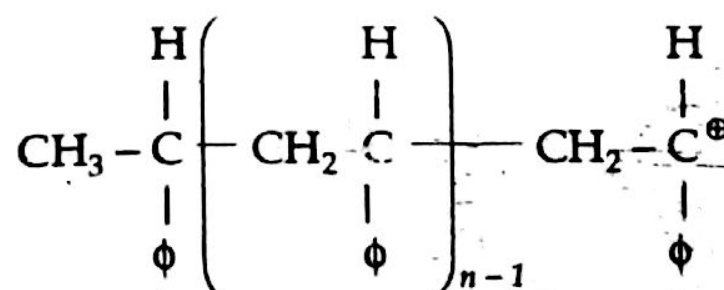
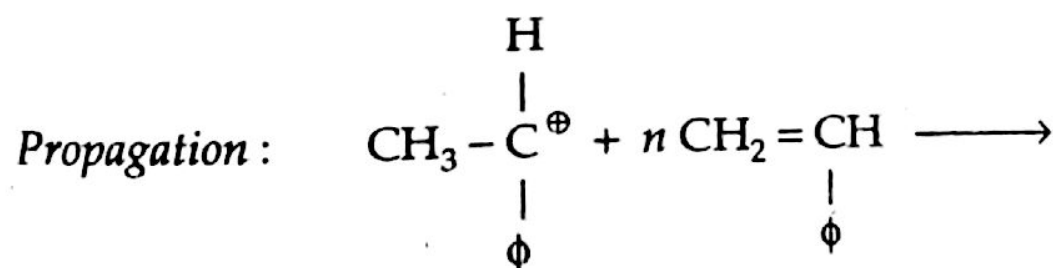
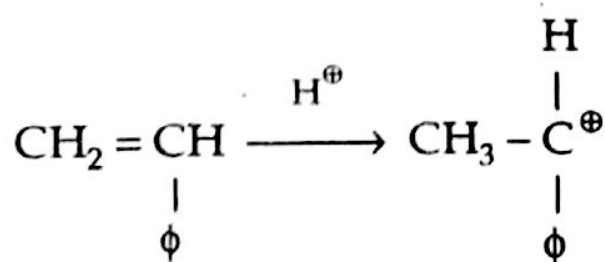
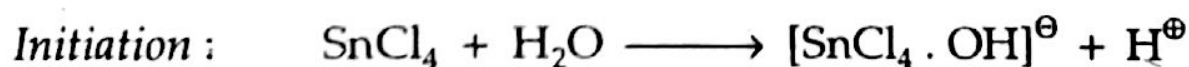
Electron releasing substituents such as alkyl, alkoxy, and phenyl increase the  $e^-$  density at the carbon-carbon double bond and facilitate its bonding to cationic species. Moreover, these substituents stabilize the carbocation intermediates in propagation steps by resonance like

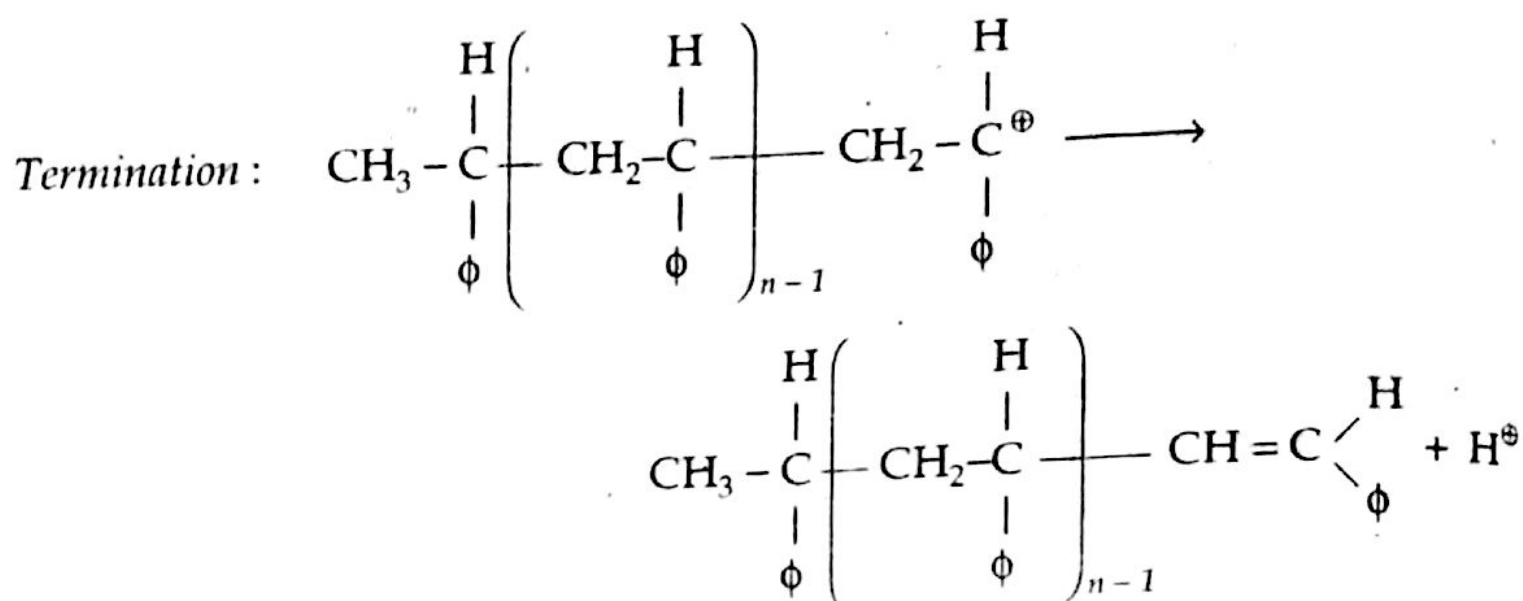


The mechanism of cationic polymerisation can be explained by the polymerisation of (a) Styrene using  $\text{SnCl}_4$  as catalyst and (b) Isobutylene using  $\text{BF}_3$  as catalyst and water as a co-catalyst (or protogen or initiator) since it supplies the proton which ultimately adds to monomer to initiate polymerization. (Note that  $\text{BF}_3$  alone cannot start the polymerization).

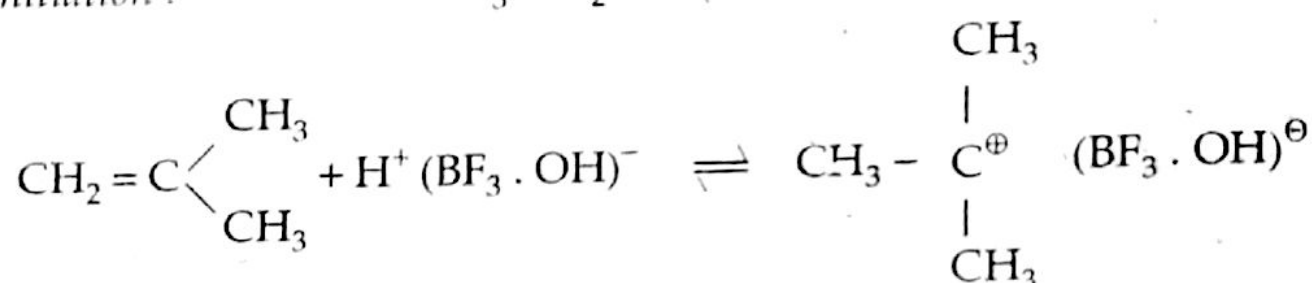
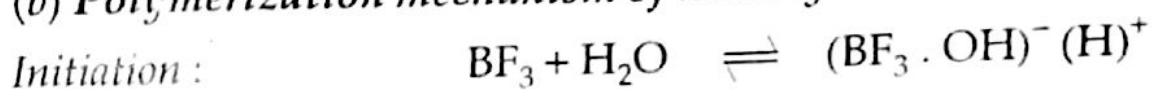


where  $\phi$  stands for  $\text{C}_6\text{H}_5$

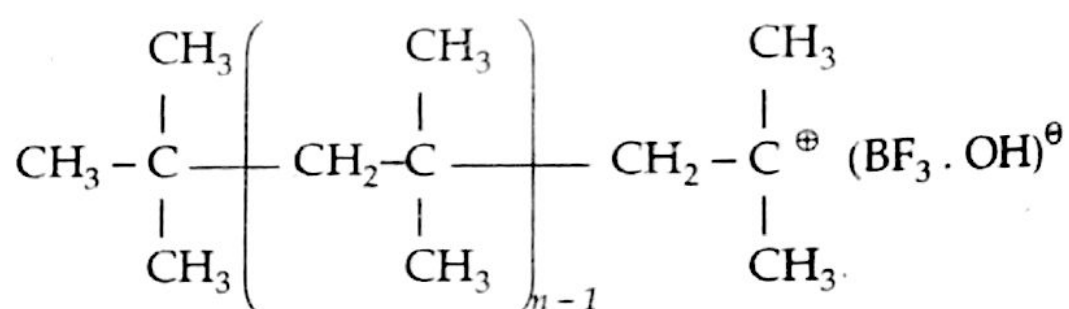
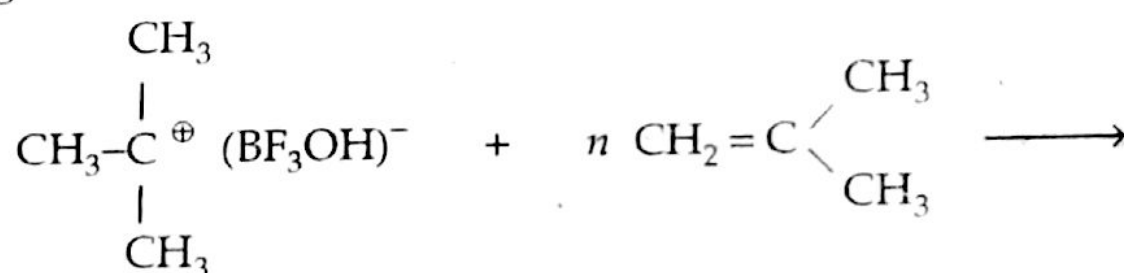




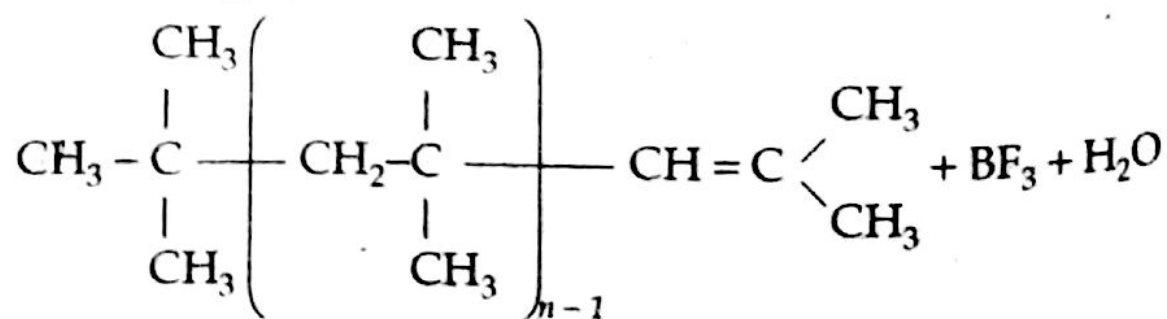
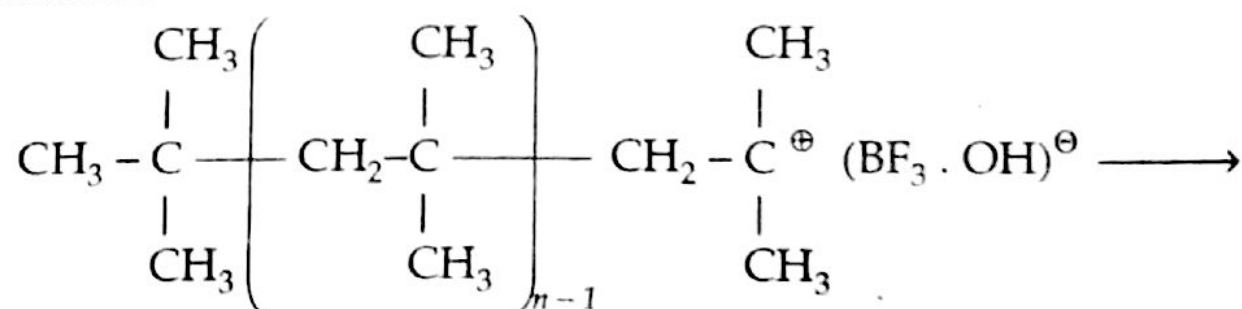
## (b) Polymerization mechanism of isobutylene



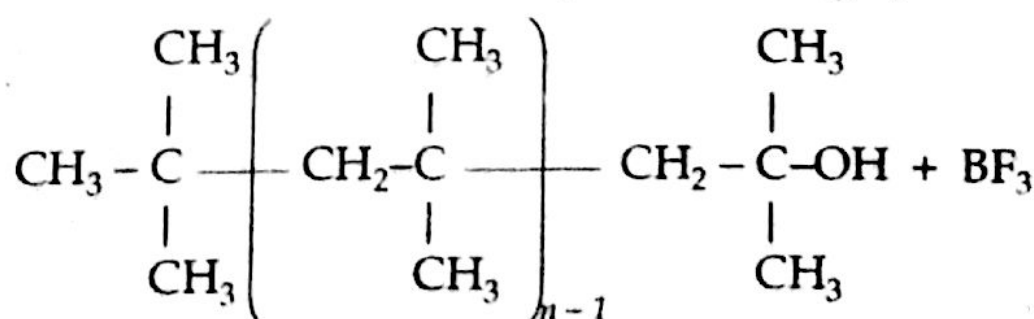
## Propagation :



## Termination :



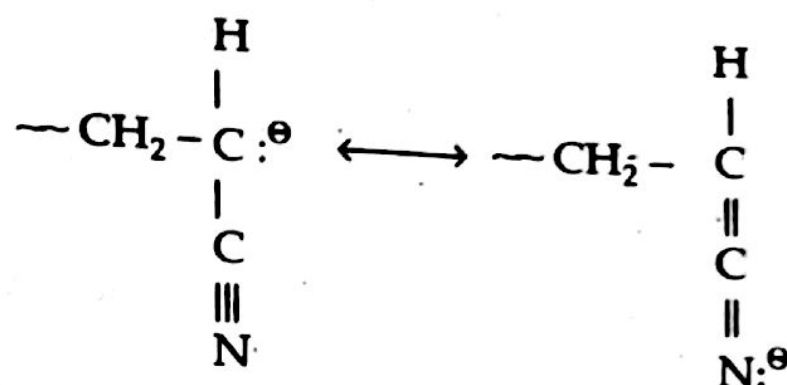
or





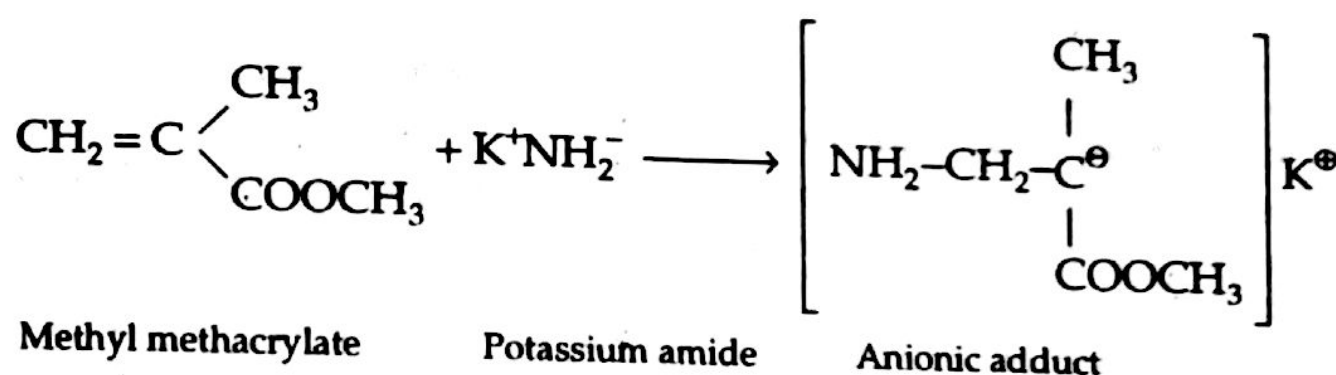
**(B) Anionic Polymerisation.** Monomers with electron attracting substituents (such as  $-\text{CN}$ ,  $-\text{COOCH}_3$  and  $-\text{C}_6\text{H}_5$  etc.) undergo anionic polymerization in the presence of sodium or potassium amide, alkali metals (such as Na, K) and Grignard reagent as catalysts. Thus, strong bases are typical catalysts.

**Mechanism.** In anionic Polymerisation, the catalyst interacts with the monomer to generate a carbanion as the active centre for chain growth. As the intermediate carbanion is stabilized by electron-withdrawing substituents hence anionic polymerization is favourable with the monomers having such substituents. For example,

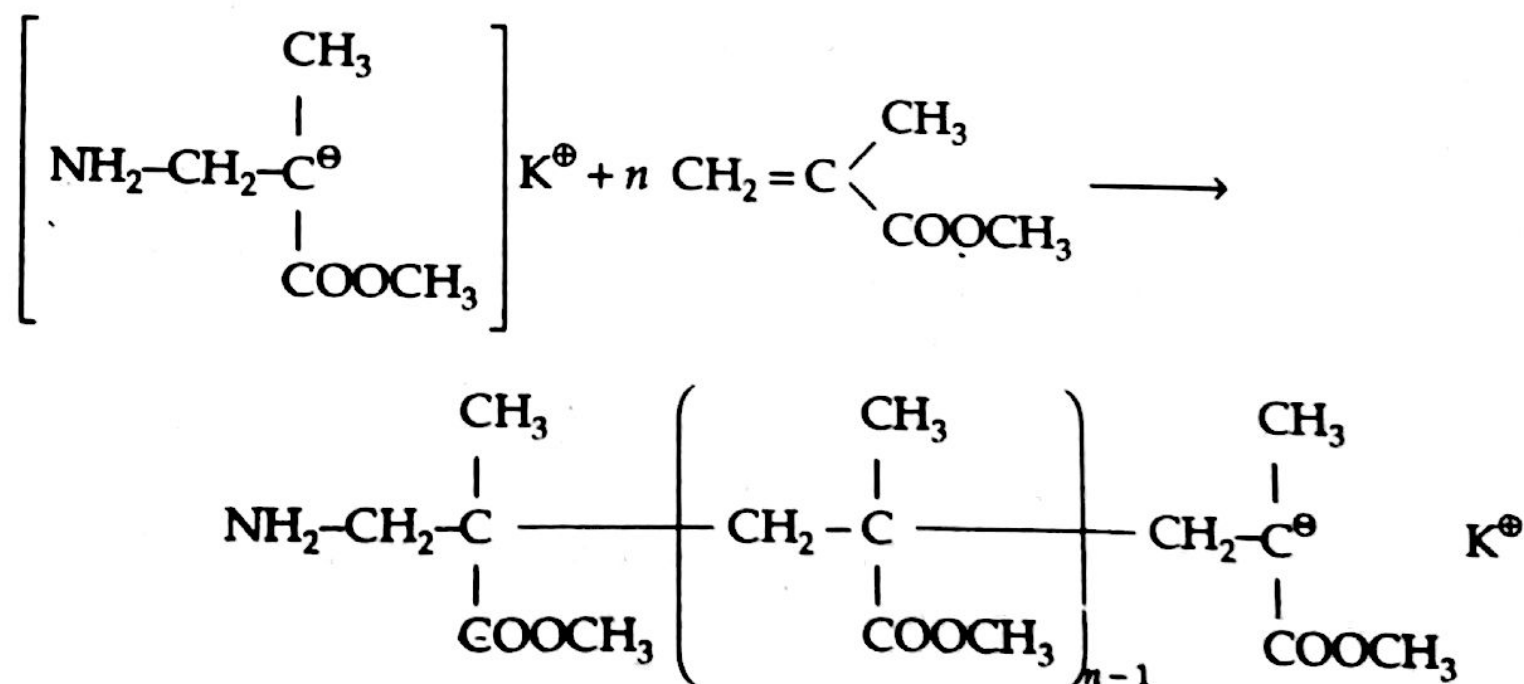


The mechanism can be explained by considering the steps for the formation of polymethyl methacrylate (PMMA) starting from methyl methacrylate.

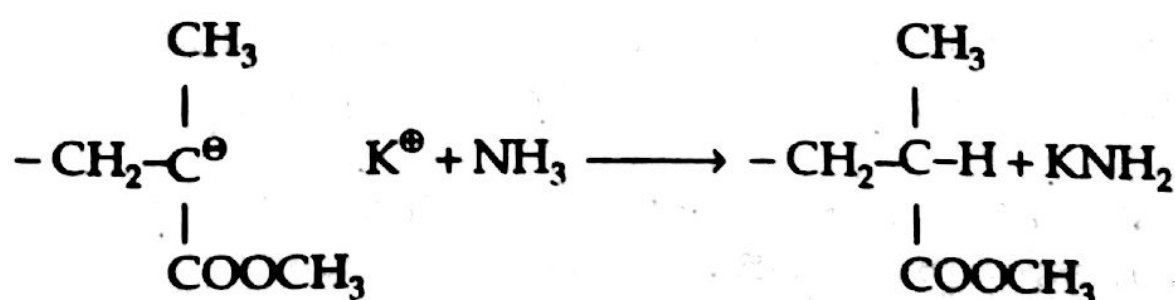
**Initiation :**



**Propagation :**



**Termination :**



The following important points can be concluded from the generalized anionic mechanism for the formation of PMMA :

(i) In anionic polymerization, the end group of a growing macro-molecule possesses high activity and good stability. The polymerization process continues till all the available monomers are consumed. Later when a fresh batch of monomer is added, polymerization process again starts. Thus the polymers are known as *living polymers*.

(ii) It is possible to produce very high molecular weight polymers by anionic polymerization.

(iii) It is also possible to produce a polymer of desired low molecular weight by stopping the polymerization at the pre-determined stage with the help of suitable terminating agent such as water. The resultant macromolecule is known as "Killed Polymer". Generally such a polymer has usually narrow molecular weight distribution.

(iv) *Block copolymers* can also be made by anionic polymerization by carefully adding alternatively the required monomers with predetermined concentration so that blocks of desired lengths are obtained.

**Notes.** (1) Ionic polymerizations are usually carried out at lower temperatures (around 0°C) than radical polymerizations (around 50°C).

(2) Ionic polymerizations are very sensitive to changes in the polarity and solvating ability of the reaction media and counter ion effects. Radical polymerizations do not show such effects.

(3) Styrene,  $\alpha$ -methyl styrene and 1, 3-butadiene monomers can be polymerized by anionic, cationic or free-radical polymerizations.

(4) *Living polymerizations* are polymerizations in which propagating centers do not undergo either transfer or termination reactions.

## 7 FIBERS

### 7.1 Polyamides

Synthetic fiber forming polyamides are also termed as 'Nylons'. The important polymers of this category are discussed below :

**Manufacture of Nylon 6.** The polyamide 'Nylon 6' is obtained from petrochemical 'cyclohexane'. First cyclohexane undergoes oxidation to produce cyclohexanone in reactor 1. Then it reacts with *hydroxylamine* in reactor 2 to form oxime. The oxime undergoes Beckmann rearrangement in presence of sulphuric acid to form *caprolactum* in reactor 3. The caprolactum on heating with small amount of water undergoes hydrolysis to produce *amine caproic acid* which on further heating in reactor 4 undergoes self condensation polymerization. In this reactor 4, water is continuously removed to get continuous supply of polymer "Nylon 6".

Thus, there are *four* steps for the synthesis of Nylon-6 starting from cyclohexane. These steps are summarized on next page.

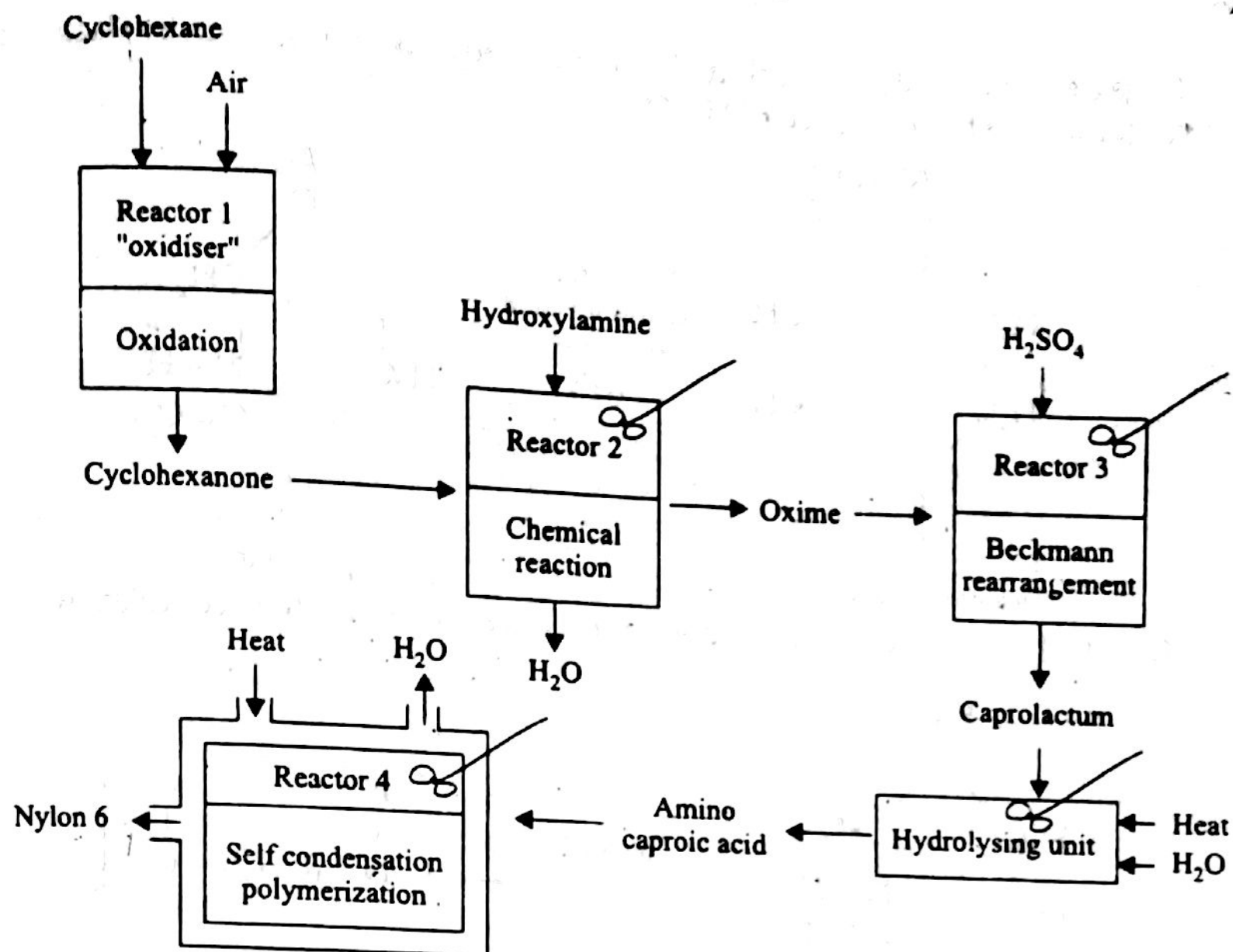
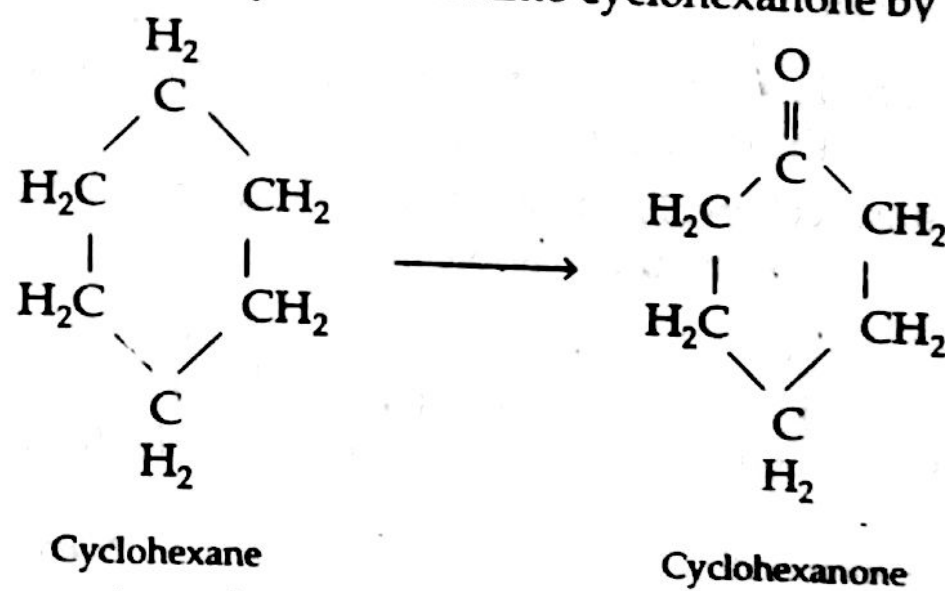
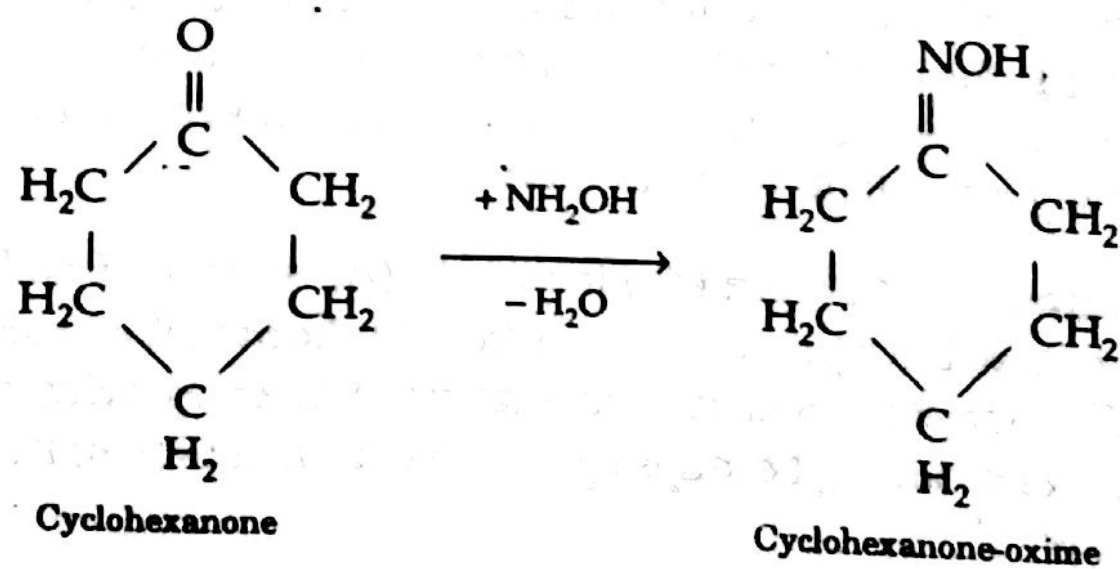


Fig. 3. Flow sheet for the manufacture of Nylon 6.

**Step (i)** Conversion of Cyclohexane into cyclohexanone by oxidation

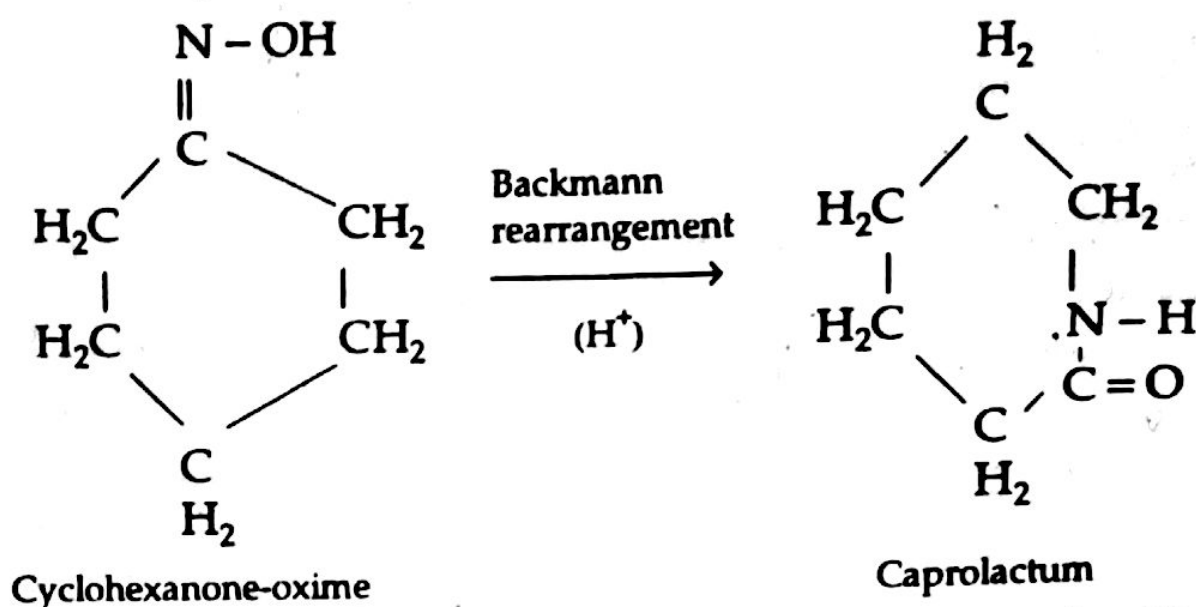


**Step (ii)** Conversion of cyclohexanone into cyclohexanone-oxime by treatment with hydroxylamine  $\text{NH}_2\text{OH}$ .

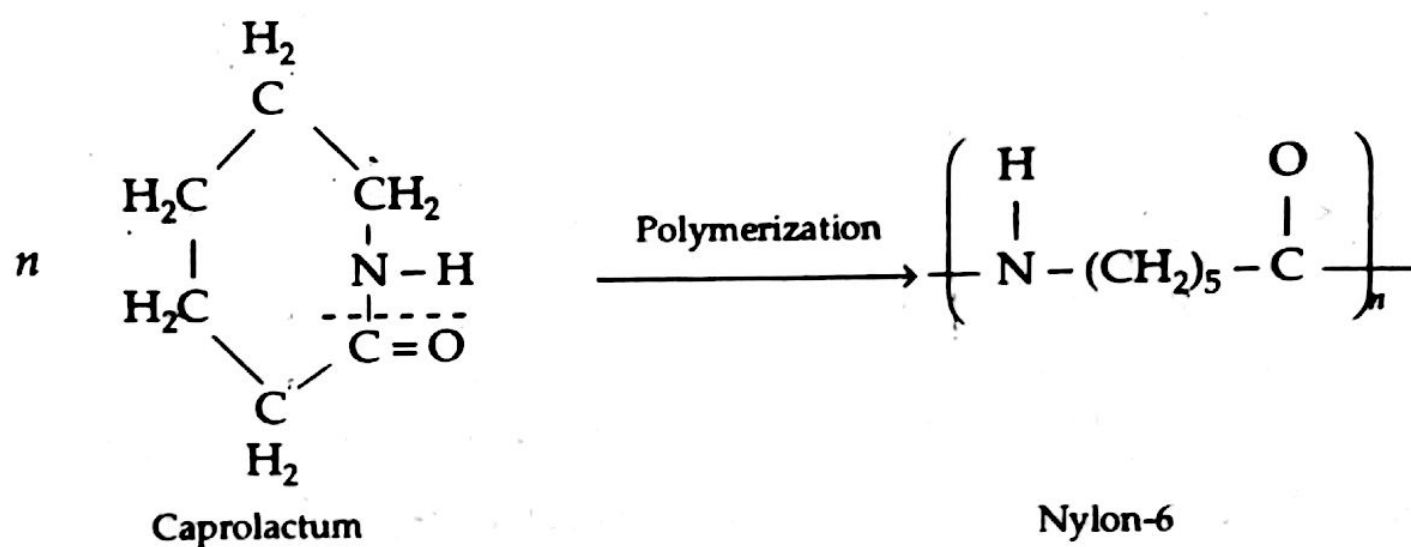




**Step (iii)** Conversion of cyclohexanone-oxime into caprolactum by Backmann rearrangement in the presence of  $\text{H}_2\text{SO}_4$

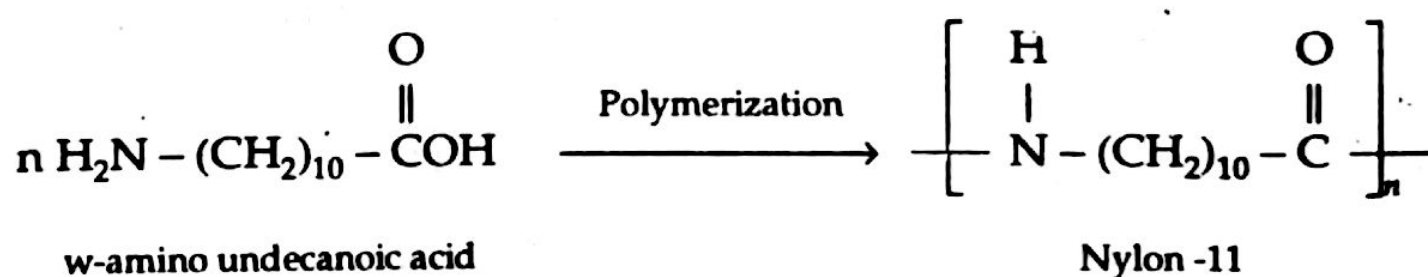


**Step (iv).** Ring opening polymerization of caprolactum to give Nylon-6.



These nylons are designated by numbering system which indicates the number of carbon atoms in the monomer chains.

To illustrate this, Nylon-11 has total 11 carbon atoms and is made by self-condensation reaction of  $\omega$ -amino undecanoic acid.



Nylons can also be made by the condensation reaction between diamines and dicarboxylic acid. These polymers are designated by two numbers. The first number represents the number of carbon atoms in diamine and second number represents the number of carbon atoms in dicarboxylic acids. There are two commercially important nylons of this type :

**Manufacture of Nylon 66.** First of all, (A) *Adipic acid* and (B) *hexamethylene diamine* are mixed in equimolar proportion. On heating they react in absence of air to form (C) *hexamethylene diammonium adipate*, known as **nylon salt**. (Fig. 4) In this step, amine and carboxyl groups condense to form amide linkage with the evolution of water.

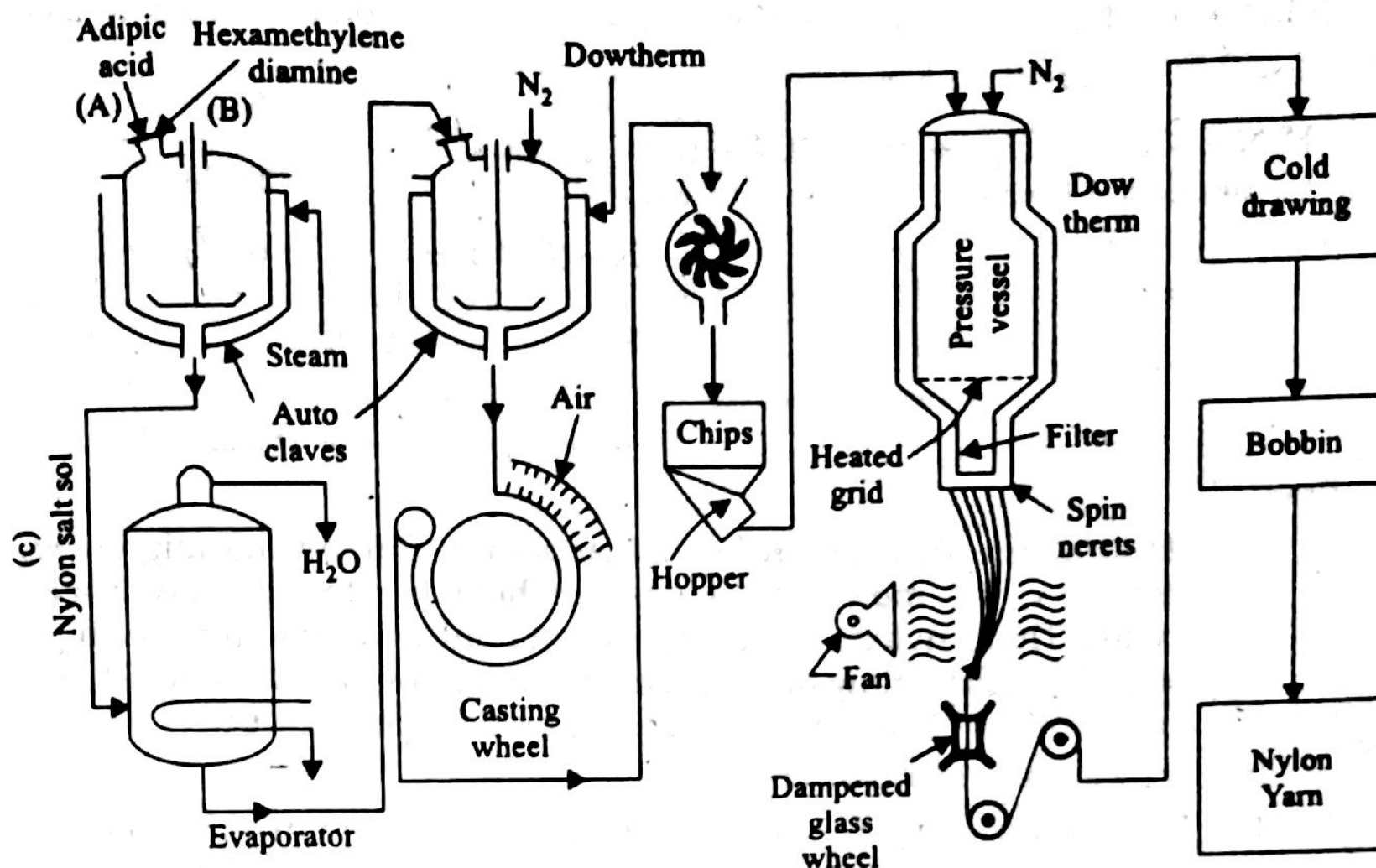
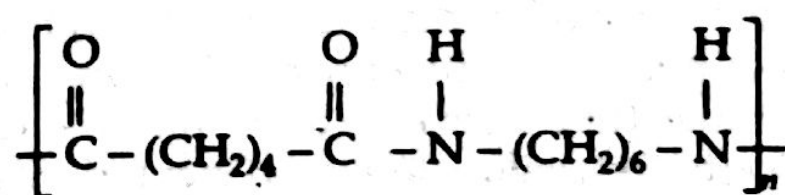
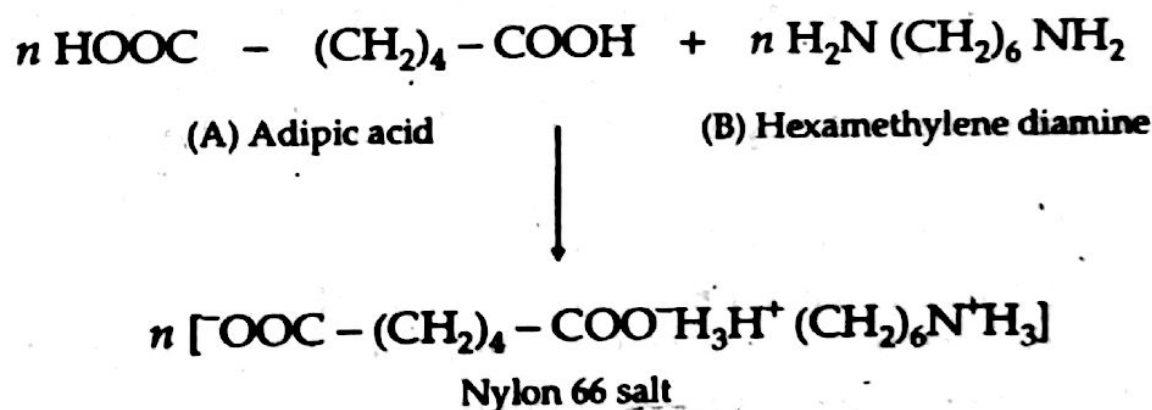


Fig. 4. Flowchart for Nylon Yarn.

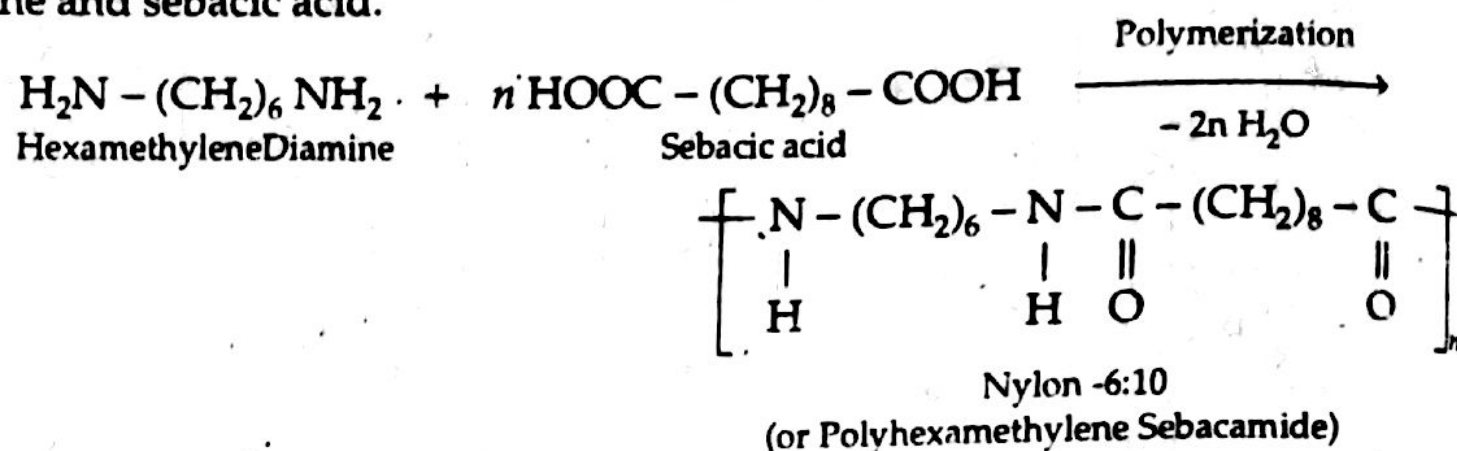
The water is removed from the nylon salt in evaporator. The dry nylon salt on further heating in presence of  $\text{TiO}_2$  yields nylon 66 polymer. This molten viscous polymer is forced out of the bottom on to a casting wheel by specially purified nitrogen gas at 175 to 345 kPa. A ribbon is formed which is cut into chips. The chips are dried in hot air. The chips are then extruded in  $\text{N}_2$  atmosphere to form filaments. The filaments after cold drawing yields nylon yarn.

The involved chemical reactions are as follows :



Nylon 66 polymer

**Nylon 6 : 10.** It is made by the condensation polymerization of hexamethylene diamine and sebacic acid.



**Properties.**

- (a) The structure of nylons are linear that permits side-by-side alignment. Moreover, the molecular chains are held together by Hydrogen bonds. Thus, nylons have high crystallinity which imparts high strength, high melting point, elasticity, toughness, abrasion resistance and retention of good mechanical properties upto 125° C.
- (b) They are also sterilisable.
- (c) Since nylons are polar polymers they have good hydrocarbon resistance. Larger the number of carbon atoms, greater will be ease of processing and hydrocarbon & moisture resistance.

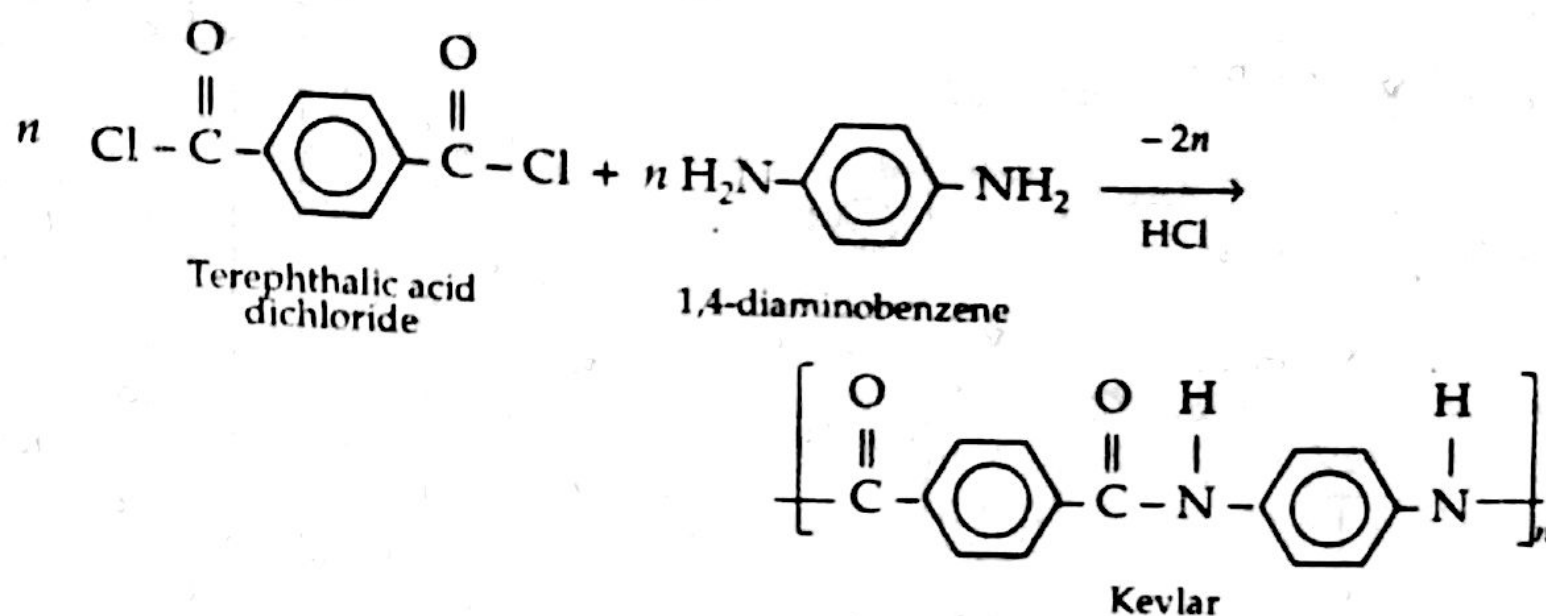
**Applications :**

- (a) Nylon-6:6 is primarily used for fibers, which find use in making socks, under-garments, carpets etc.
- (b) Nylon 6:6 is also used in mechanical engineering for well known applications like Gears, Bearings, Bushes, Cams etc. Apart from advantageous properties listed above, Nylon moving parts may be frequently operated without lubrication. They are silent running and may often be moulded in one piece when previously a metal part required assembling of several parts or alternatively extensive machining with consequent waste of material.
- (c) Nylon 11 and Nylon 12 are used for making flexible tubings for conveying petrol.
- (d) Mouldings having application in medicine and pharmacy because of sterilisability.
- (e) Durable (but costly) hair combs.
- (f) Nylon 6:6 is also used for jacketing electrical ware to provide a tough, abrasion resistant outer cover to protect the primary electrical insulation.
- (g) Nylon 6 is mainly used for making tyre cords.
- (h) Nylon 6:10 is suitable for monofilaments which are used for bristles, brushes etc.
- (i) Glass reinforced Nylon plastics are used in housings and casings of domestic appliances, radiator parts of car and for relay coil formers (in telecommunication field). [These plastics are characterized by rigidity, creep-resistance, low coefficient of friction, high heat deflection temperature, good low frequency electrical insulation properties and non-magnetic characteristics].



**Kevlar**

**Preparation.** It is prepared by the condensation polymerisation of terephthalic acid dichloride and 1,4-diaminobenzene.



**Properties.** As can be seen from the repeat unit structure of kevlar, benzene rings are linked to the amide linkage, therefore kevlar is very rigid polymer. There are stronger intermolecular forces between neighbouring chains which make it exceptionally strong. It also has high heat stability.

**Applications.** Kevlar has following potential uses :

- (a) Tyres, brakes, clutch lining and other car parts ;
- (b) Bullet-proof vests ;
- (c) Motor cycle helmets ;
- (d) Aerospace and air-craft industries.

## 7.2 Polyethylene terephthalate (PET)

From Commercial point of view, poly ethylene terephthalate (PET) is the most important polymer of this class. It is also known as terylene or Dacron.

**Manufacture of Dacron.** Dacron or terylene or polyethylene terephthalate (PET) is prepared from terephthalic acid, methyl alcohol and ethylene glycol. First, terephthalic acid is obtained by the oxidation of *p*-xylene in autoclave reactor (1), refer Fig. 5. Terephthalic acid obtained is further treated with methyl alcohol at 150°C in esterification reactor (2), using sulphuric acid as a catalyst. The product, dimethyl terephthalate (DMT) is purified by crystallization and distillation. Then this purified dimethyl terephthalate (DMT) is reacted at 230°C with ethylene glycol in transesterification reactor (3) so as to get dihydroxy dimethyl terephthalate (called as "ester monomer"). The Dacron formation from this ester monomer proceeds in two steps. In the first step, done in low polymerizer (4), low molecular weight polyester is formed along with glycol. Then temperature is slightly raised and pressure is lowered to remove glycol. The reaction conditions in high polymerizer (5) are adjusted so as bring about effective condensation. At 260 – 300°C under vacuum, terylene is formed in high polymerizer. Simultaneously ethylene glycol is distilled out. Terylene is then extruded and from direct spinning system, PET fiber is obtained.

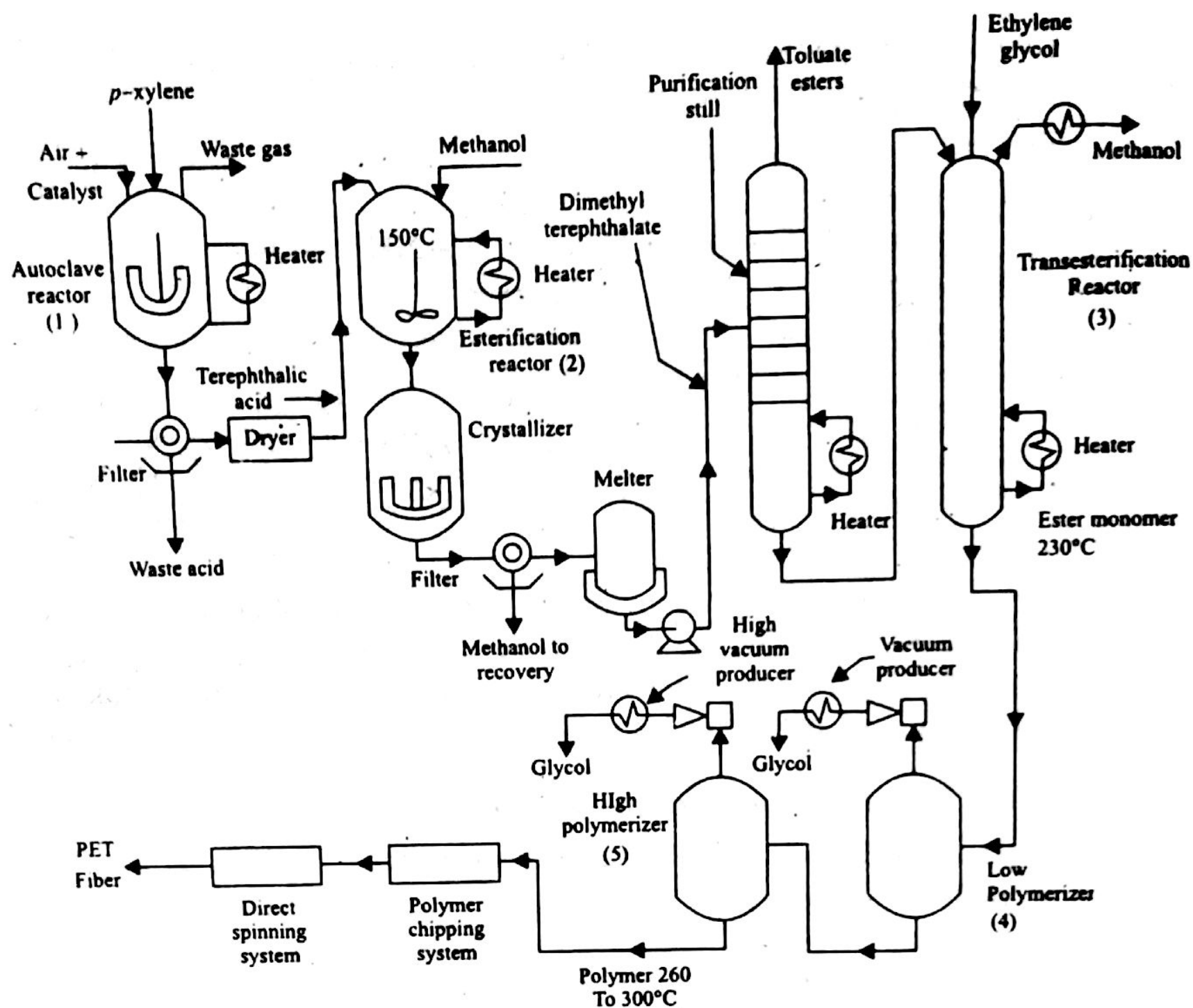
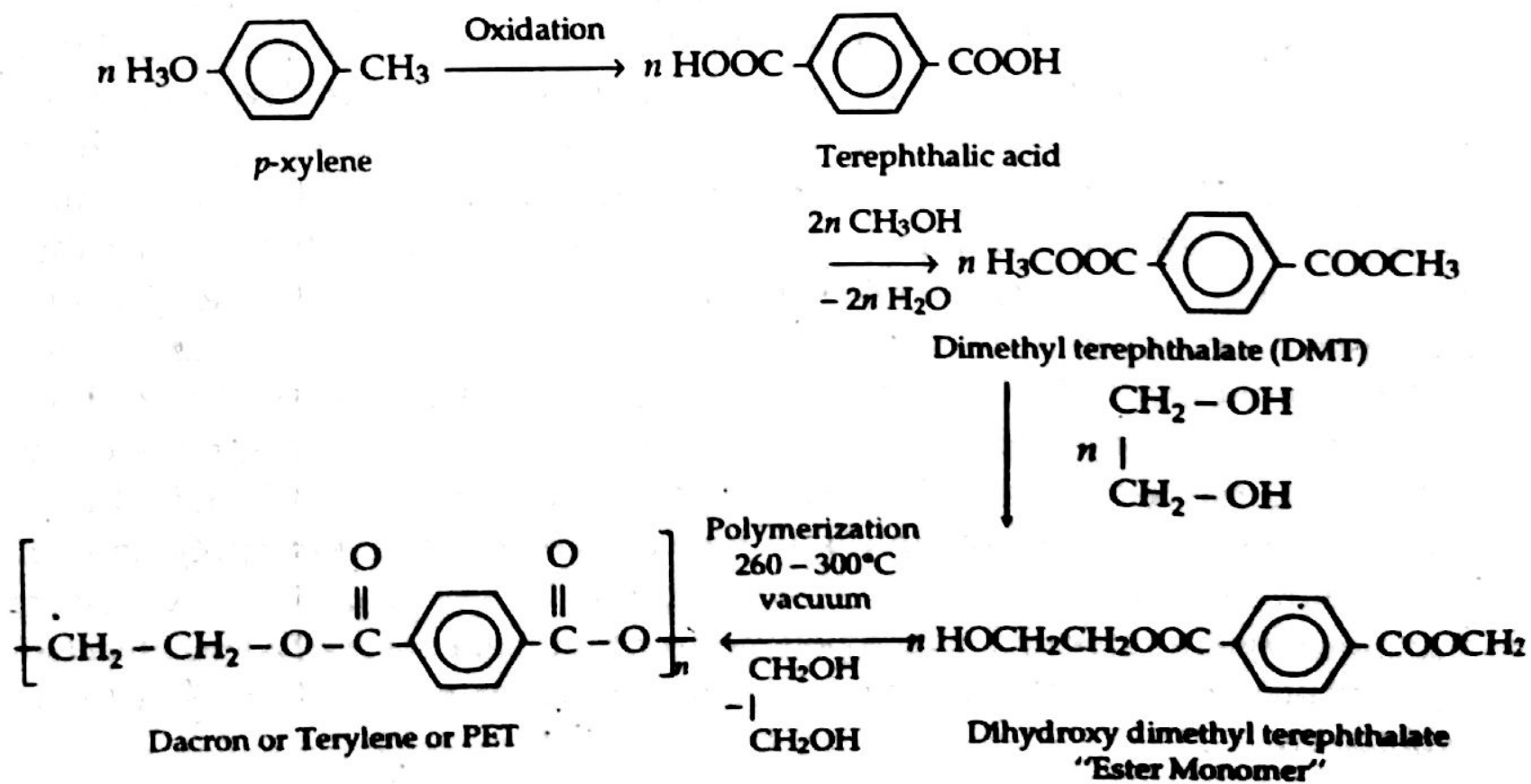


Fig. 5. Flowsheet for Dacron.

The chemical reactions involved are as follows :



### Properties.

- (a) The polyethylene terephthate readily crystallises because of the symmetrical structure and numerous polar groups. Its  $T_g$  and  $T_m$  are  $80^\circ\text{C}$  and  $265^\circ\text{C}$  respectively ;
- (b) It has good resistance to hydrocarbon solvents and moisture.
- (c) It has good mechanical properties like high modulus, tensile strength, tear strength and impact strength which are retained up to  $150 - 175^\circ\text{C}$ . These properties are derived from stiff polymer chain and powerful dipole-dipole attractions.
- (d) It is a good fiber forming material, and fibers have outstanding crease resistance, low moisture absorption and they are more durable.
- (e) Biaxially oriented films and bottles are transparent. They also have excellent strength and barrier properties.
- (f) Glass filled PET mouldings have superior mechanical properties and high temperature resistance.
- (g) Blends of terylene fibers with wool have better crease and wrinkle resistance, they are more durable, they have higher strength, they do not shrink and are not attacked by moths. The blends also have better finish.

### Applications.

- (a) Magnetic recording tape.
- (b) Films are used for making transparency of overhead projector. Bottles are used for Cola-drinks Fruit juice concentrates and sauces.
- (c) Wide-necked jars for coffee.
- (d) Glass filled PET mouldings are used for the housings for toasters, coffee machines, car heater and water meter.
- (e) Terylene fibers are also used for blending with wool.

## 7.3 Cellulose Fibres

### 7.3A Viscous Rayon

#### Manufacture of Cellulose Fibre (Viscose Rayon) :

First of all, (A) *cellulose material* (pulp) is charged in a **steeping press** (1) and is steeped either batch wise or continuously in (B) *caustic soda* ( $\text{NaOH}$ ) solution ( $17 - 20\%$ ) for 1 hour at  $13 - 17^\circ\text{C}$ . After this step (C) *sodium cellulose* (or alkali cellulose) is formed excess liquor is drained off (Refer Fig. 6).

In second step, alkali cellulose is treated with *carbon disulphide* (D) in **xanthating churn** (2) to form (E) *cellulose xanthate*.

Cellulose xanthate is further treated with dilute caustic soda solution in **dissolver** (3) so as to get a viscous colloidal dispersion called (F) *viscose liquid* which is ripened for 4 - 5 days. This is then transferred into **viscose tank** (4) through filter presses. Viscous solution is filtered to remove foreign bodies and then vacuum debubbling is done to remove bubbles. Finally ageing is done to adjust the final viscosity.



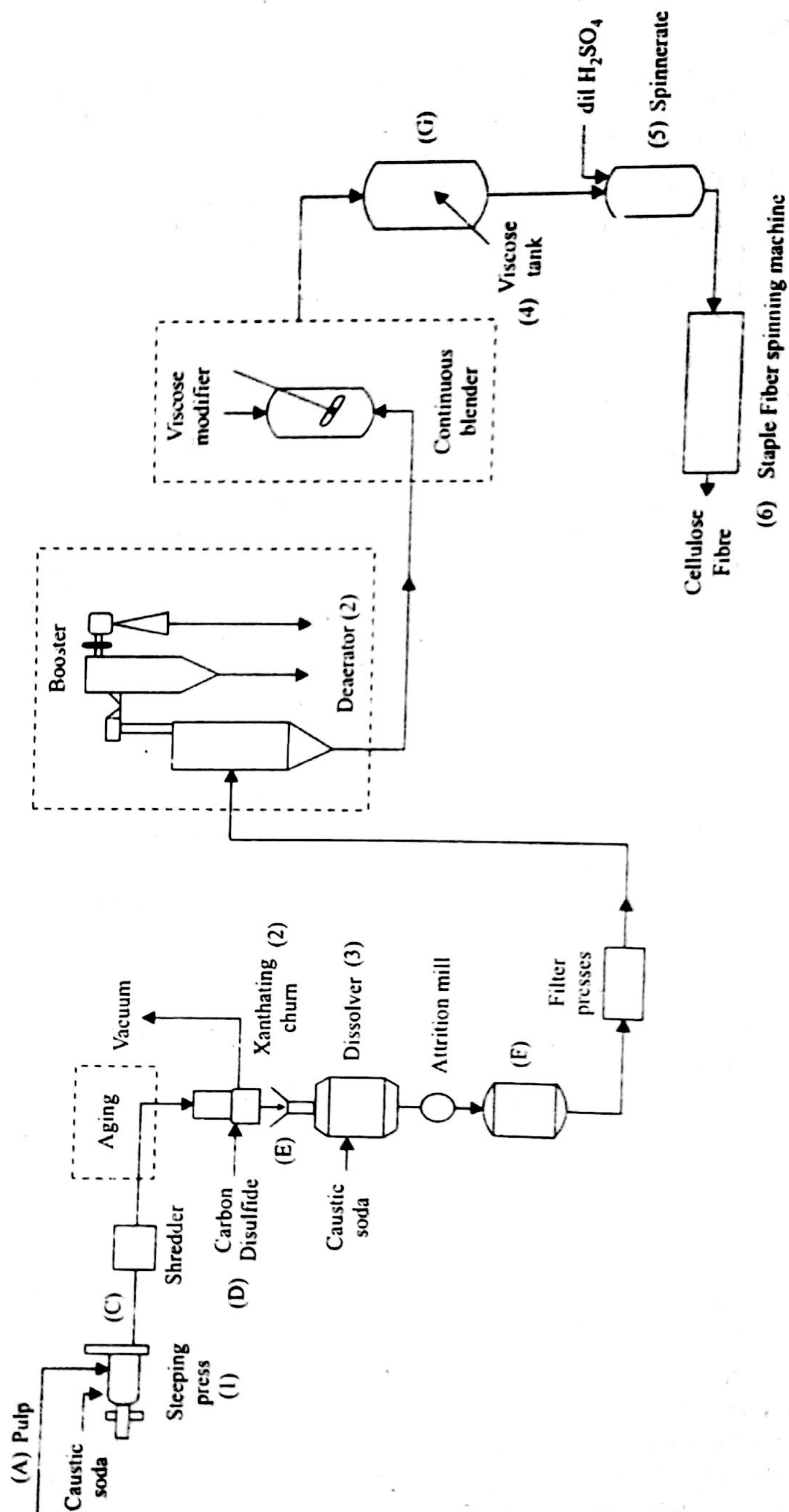


Fig. 6. Flow sheet for cellulose fibre.

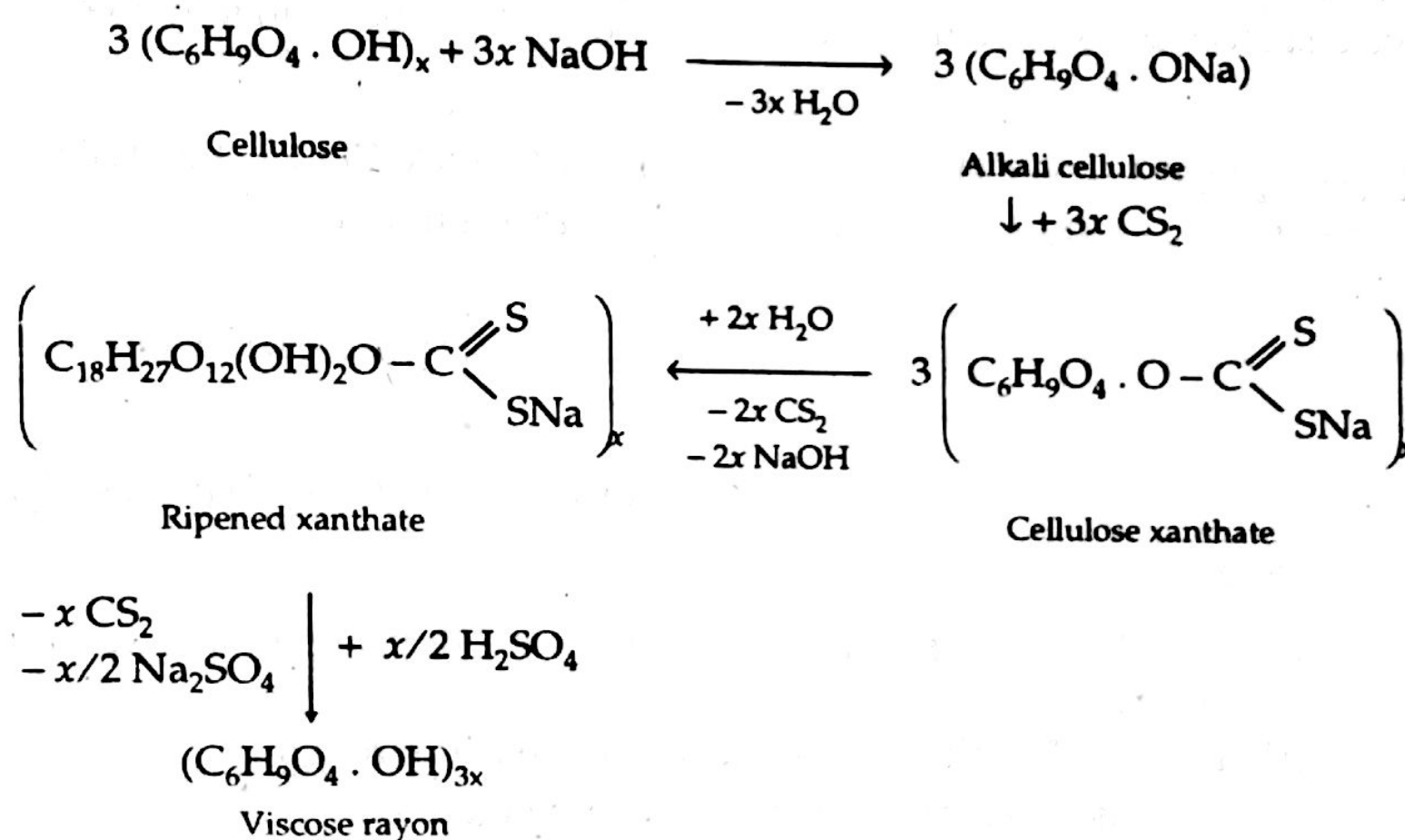
The filtrate containing viscose alkali cellulose xanthate is extruded through spinnerets (small holes) into the acid bath. In this process cellulose xanthate is hydrolysed to cellulose and fibers are formed. The fibers of regenerated cellulose are washed, desulphurised, bleached and re-washed to remove traces of all the chemicals and finally dried.

These dried fibers can be either sold in the form of continuous filament yarn (known as **viscose rayon yarn**) or cut into short lengths before drying (in this case, they are called **staple fibre**). These short staple fibres are very useful for blending with other fibers and spinning into threads.

To Sum up,

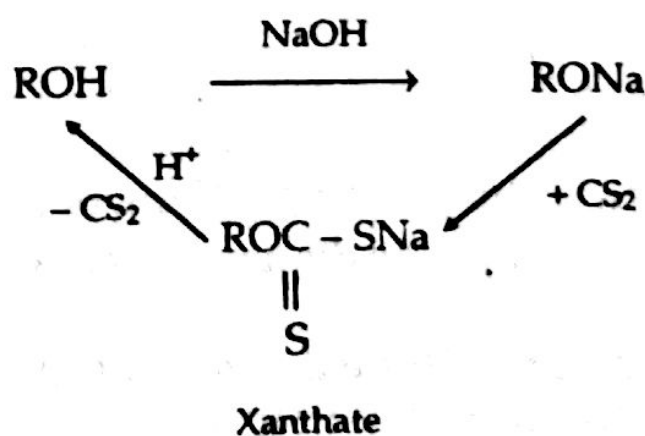
**Rayon** is the generic name given to fibres (filaments cut into small lengths) and continuous filament yarns made of regenerated cellulose.

The involved chemical reactions are as follows :



### Do you know!

When an alcohol is treated with aqueous sodium hydroxide and carbon disulfide, a compound called xanthate is obtained. Treatment of the xanthate with aqueous acid regenerates the starting materials.

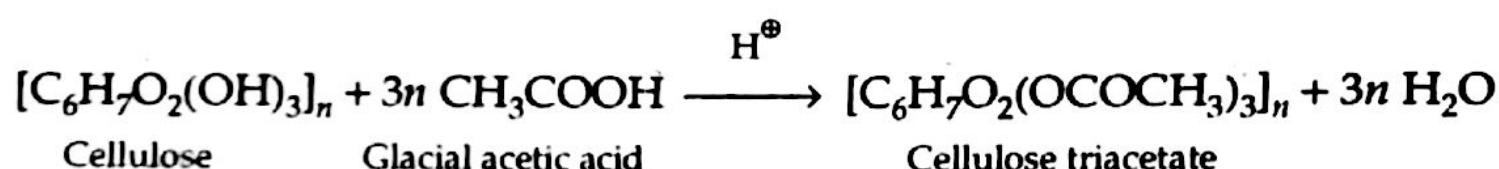


**Properties of Cellulose fibres.** Cellulose fibres have fine lusture, and low tensile strength. They can tolerate ironing temperature. They can absorb upto 20% moisture. There is no effect of dilute alkalies on them but concentrated alkali saponify them. Dilute acids at room temperature slowly react and weaken the fibre. However, at high temperature, acid react vigorously and decompose them.

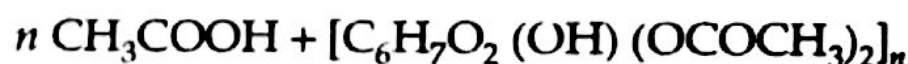
**Applications.** Cellulose fibres are used as a substitute of cotton in textile industry.

### 7.3B Cellulose Acetate

**Preparation :** It is made by reacting natural cellulose with acetic anhydride (or glacial acetic acid) in the presence of a catalyst (such as sulphuric acid). Estrification reduces the molecular weight of cellulose to about 300-400 units. The triacetate of cellulose is insoluble in acetone. It is partially hydrolysed so that about 2 to 2.5 acetyl groups per  $C_6H_{10}O_5$  units remains & the product becomes soluble in organic solvent such as acetone. Solutions of cellulose acetate can be spun into fibers.



↓  $n H_2O$  (Hydrolysis)



**Properties :**

- (a) Cellulose acetate has good clarity, stability, toughness & impact strength.
- (b) It has high dielectric strength & high tensile strength.
- (c) It has good resistance to U.V. and mineral acids.

**Applications :**

- (a) Cellulose acetate is used for preparing fibers for textiles on one hand and preparing transparent sheets on the other.
- (c) Films are also used for making small envelops, bags & boxes for packaging.

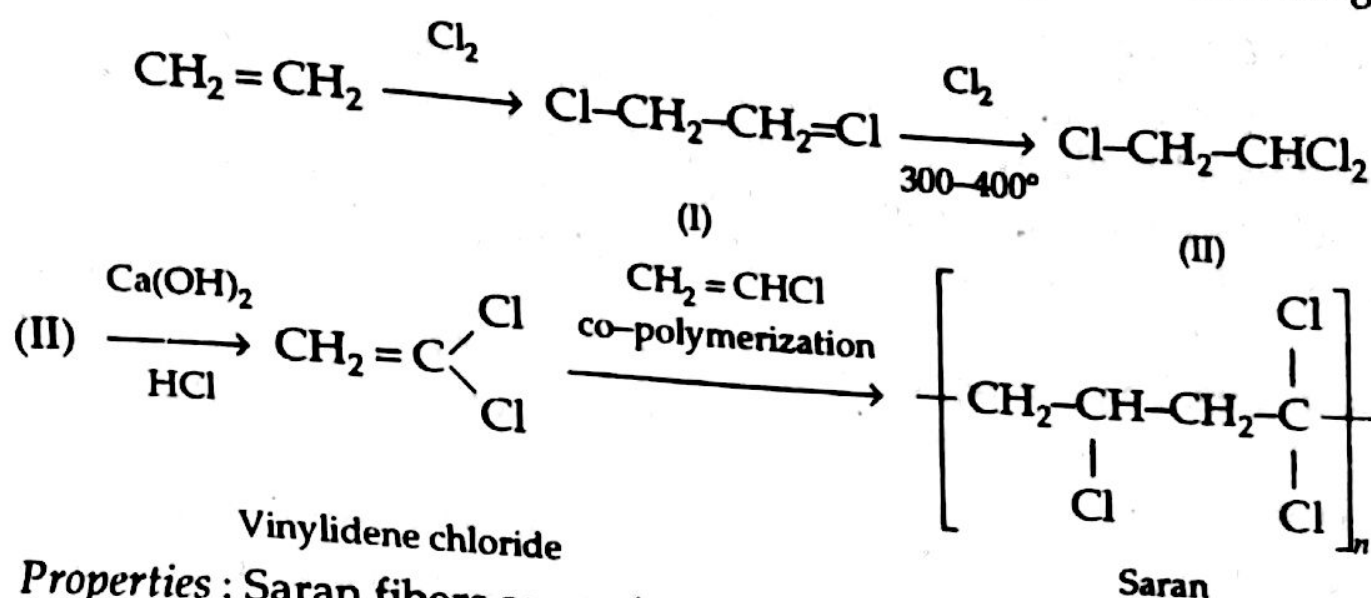
### 7.4 Polyvinyls

Commerically there are two fibre forming polymers which come under this category. They are Saran & Vinyon and are discussed below :

(i) **Saran.** Saran is the trade name of the copolymer of 90% vinylidene chloride ( $CH_2 = CCl_2$ ) and 10% vinyl chloride ( $CH_2 = CHCl$ ).



**Preparation :** It is obtained from ethylene according to the following series of reactions :

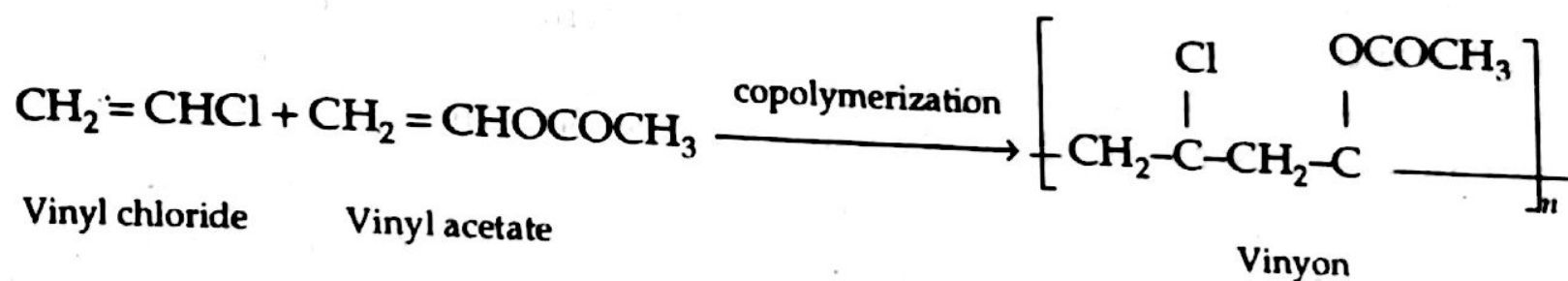


**Properties :** Saran fibers are resistant to fire and most of the chemical reagents.

**Applications :** Saran fibers are used for the manufacture of autoseat covers, window screens, drapes etc.

(ii) **Vinyon.** Vinyon is the copolymer of vinyl chloride and vinyl acetate.

**Preparation :**



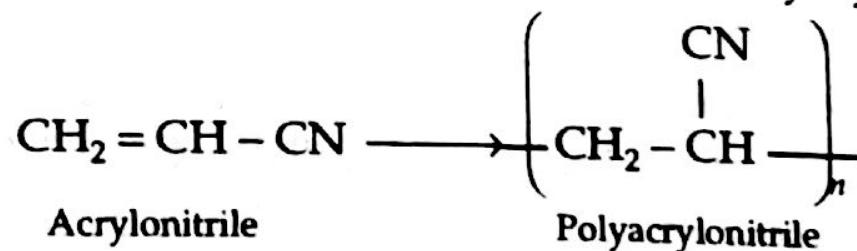
**Properties :** Vinyon fibre is characterized by remarkable resistance to the chemical reagents & it has thermoplastic nature.

**Applications :** Vinyon fibre is used in textile industry & in the manufacture of felts.

## 7.5 Acrylonitriles (or Orlon)

Orlon is the trade name of polyacrylonitrile.

**Preparation :** It is made by the polymerization of vinyl cyanide.



**Properties :** Polyacrylonitrile softens only slightly below its decomposition temperature of about 300 °C so it found little use as a plastic material. Moreover, it does not dissolve in its monomer so it cannot be shaped by bulk casting.

As it dissolves in solvents such as dimethylformamide and tetramethylenesulphone so it found wide use as fibers. *Orlon* is the trade name of polyacrylonitrile. Orlon fibers are resistant to water and are quick drying. These are more resistant to acid, gases than nylon.

**Applications :** Orlon fibers are used for manufacturing window shades. It can also be used as wool-like fiber for suits, bathing suits, sweaters, etc.

## 8 RUBBERS/ELASTOMERS

### 8.1A Natural Rubber

**Processing of Natural Rubber.** By making small incisions on the barks of rubber trees, like *havea brasiliensis* and *gauyule*, the rubber latex can be collected into small vessels, as it oozes out. Rubber latex contain 25 to 45% of rubber in the form of milky colloidal emulsion the remainder of which is made mainly of water and small amounts of protein and resinous material. With time, the flow of latex from the cut decreases. Thus, at regular intervals, (about six months) **Tapping** (removal of another thin layer of bark) is necessary throughout the life of the tree, which is about 40 years.

Latex is diluted to contain 15 to 20% of rubber. After dilution it is filtered to eliminate any dirt that may be present. It is then coagulated in a tank fitted with irregular partitions by adding about 1 kg acetic acid or formic acid per 200 kg of rubber, to a soft white mass. Sometimes, Ammonium or potassium alum are also used as coagulants. After washing and drying, the coagulum is subjected to any of the following processes :

(i) **Crepe rubber.** It is prepared by adding little sodium bisulfite to bleach the rubber and then it is passed through a 'creping machine' so that coagulum is rolled out into sheets of about 1 mm thickness. The sheet possesses an even rough surface resembling crepe paper. The sheet is then dried at 50° C in air.

(ii) **Smoked rubber.** It is made by eliminating the bleaching with sodium sulfite and rolling the coagulum into somewhat thicker sheets having ribbed pattern on its surface. Ribbed surface pattern on the sheet prevents them from adhering together on stacking. It also facilitates consequent drying as it exposes greater surface area of the sheet. The sheets are then dried in smoke houses at about 50° C in the smoke from burning wood or coconut shells. The rubber sheet thus obtained is translucent and ambre in colour.

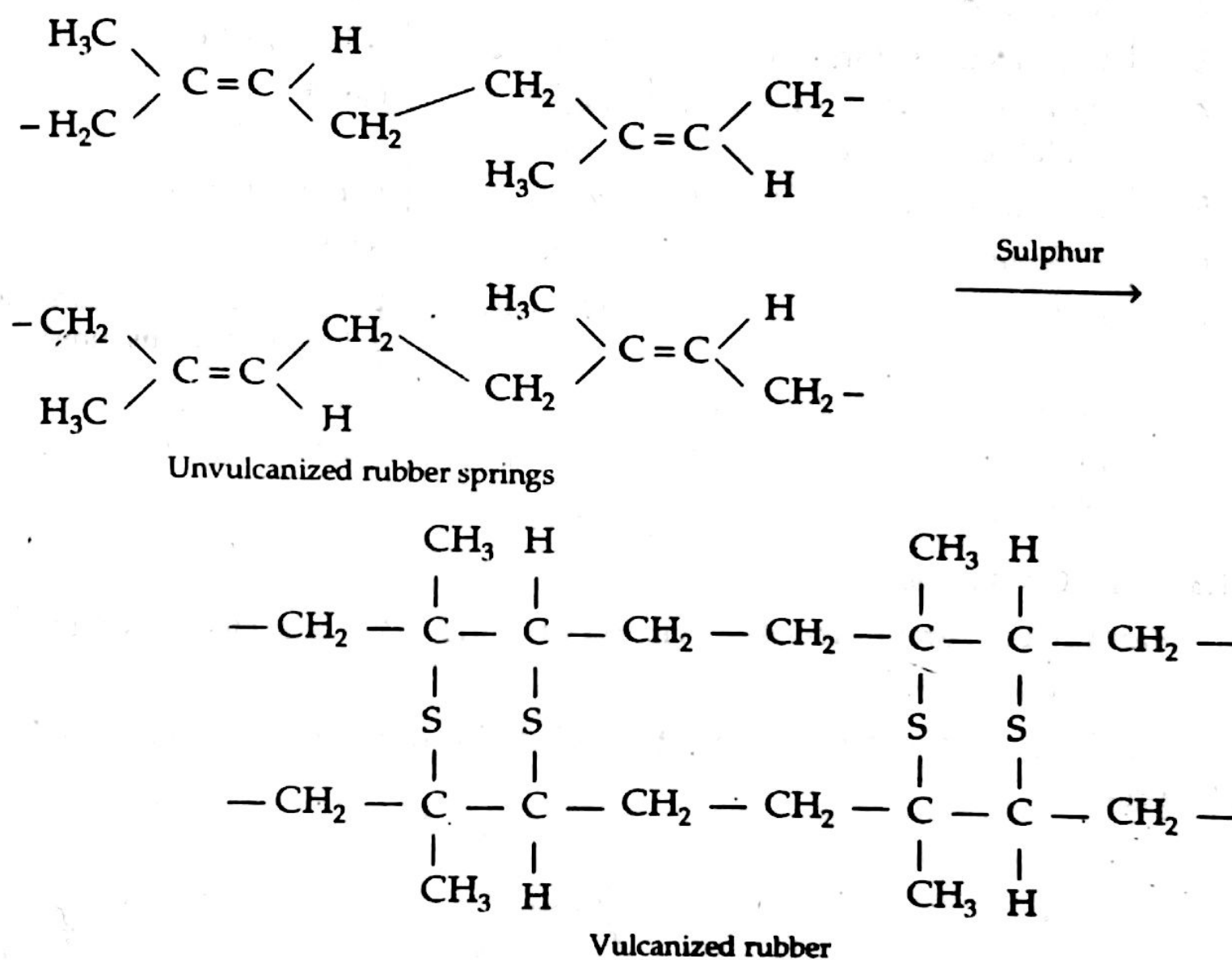
**Drawbacks of raw rubber.** These are enlisted below :

- (a) Raw or crude rubber becomes soft and sticky in hot summer, while in cold weather it becomes hard and brittle. Its usage temperature range is very limited.
- (b) It is weak, because of its low tensile strength ( $200 \text{ kg/cm}^2$ ).
- (c) It is attacked by oxidising agents ( $\text{HNO}_3$ , CONC.  $\text{H}_2\text{SO}_4$ , etc.)
- (d) In organic solvents it undergoes swelling and gradual disintegration.
- (e) It possesses tackiness, which means that under pressure two fresh raw rubber surfaces coalesce together to form a single piece.
- (f) When stretched to a great extent, some molecular chains undergo sliding or slippage over each other, hence it suffers from permanent deformation.
- (g) Due to its oxidation in air, it is not durable.

To improve the properties of rubber, it is compounded with various ingredients and the rubber mix is prepared for vulcanization. The addition of compounding agents is facilitated by the process of *mastication*. Mastication of rubber means

it is subjected to severe mechanical working. Oxidative degradation accompanied by a marked decrease in the molecular weight of the rubber occurs. This converts rubber into soft and gummy mass. Now, compounding agents are added and the rubber mix is prepared for vulcanization process.

**Vulcanization.** It consists of heating the raw rubber at  $100 - 140^{\circ}\text{C}$  with sulphur. The sulfur combines chemically at the double bonds of different rubber springs and provides cross-linking between the chains. This cross-linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs. The amount of sulphur added determines the extent of stiffness of vulcanized rubber. For example, ordinary soft vulcanized rubber (for tyres) may contain 3 to 5% sulphur, but hard rubber (say for a battery case) may contain as much as 30% sulphur.



Vulcanization of raw rubber with sulphur as vulcanizing agent.

**Advantages of vulcanization :**

- The tensile strength of vulcanized rubber is very good, about 10 times the tensile strength of raw rubber.
- It has excellent resilience (After the removal of deforming force, the articles made from vulcanized rubber regain their original shape).
- It has broader useful temperature range ( $-40$  to  $100^{\circ}\text{C}$ ) compared to raw rubber's useful temperature range ( $10$  to  $60^{\circ}\text{C}$ ).
- It has better resistance to moisture, oxidation and abrasion.



- (e) It is resistant to organic solvent like  $\text{CCl}_4$ , benzene petrol etc. but it swells in them.
- (f) It has only slight tackiness ;
- (g) It has low elasticity. (This property depends on the extent of vulcanization. Ebonite has practically no elasticity). The superior properties of vulcanised rubber compared to raw rubber are summarised below in Table 3.

Table 3. *Vulcanised rubber vs. raw rubber*

S.No.	Property	Raw rubber	Vulcanised rubber
1.	Tensile strength	200 kg/cm <sup>2</sup>	2000 kg/cm <sup>2</sup>
2.	Resilience	Good	Very good
3.	Useful temperature range	10 – 60° C	– 40 to 100° C
4.	Resistance to moisture oxidation and abrasion	Poor	Good
5.	Resistance to organic solvents	Poor	Large but limited
6.	Tackiness	Marked	Slight
7.	Elasticity	Very high	Low (and decreases with extent of vulcanisation)
8.	Percent elongation at break	1200	800
9.	Manipulatability to desired shape	Not easy	Easy

**8.1B cis-trans Rubber**

Natural rubber is cis-1,4-polyisoprene. The all trans stereoisomer occurs naturally as gutta percha.

Fig. 7(a) below compares the extended chains of natural rubber with those of gutta percha.

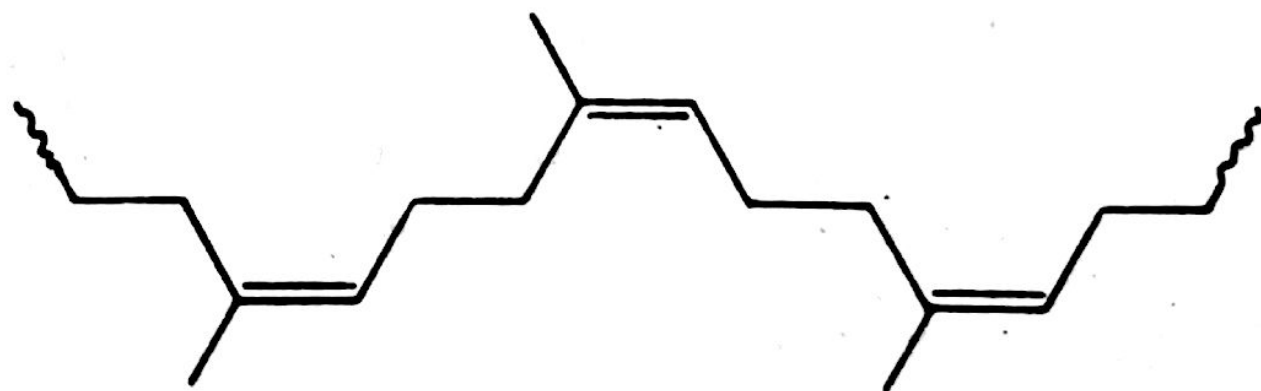


Fig. 7. (a) Natural rubber, cis-1,4-polyisoprene

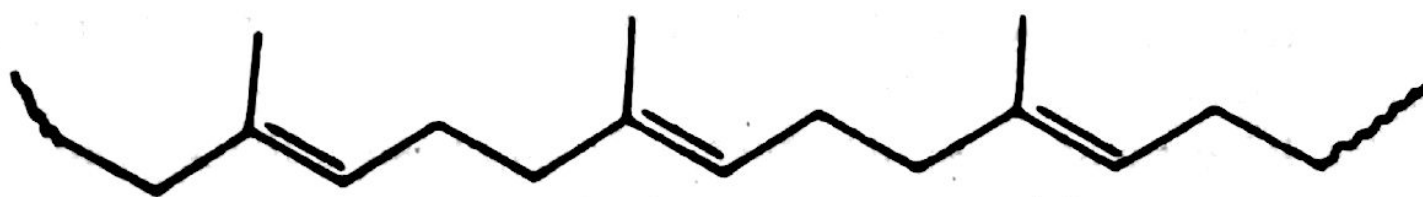


Fig. 7. (b) Gutta percha, trans stereoisomer of (a).

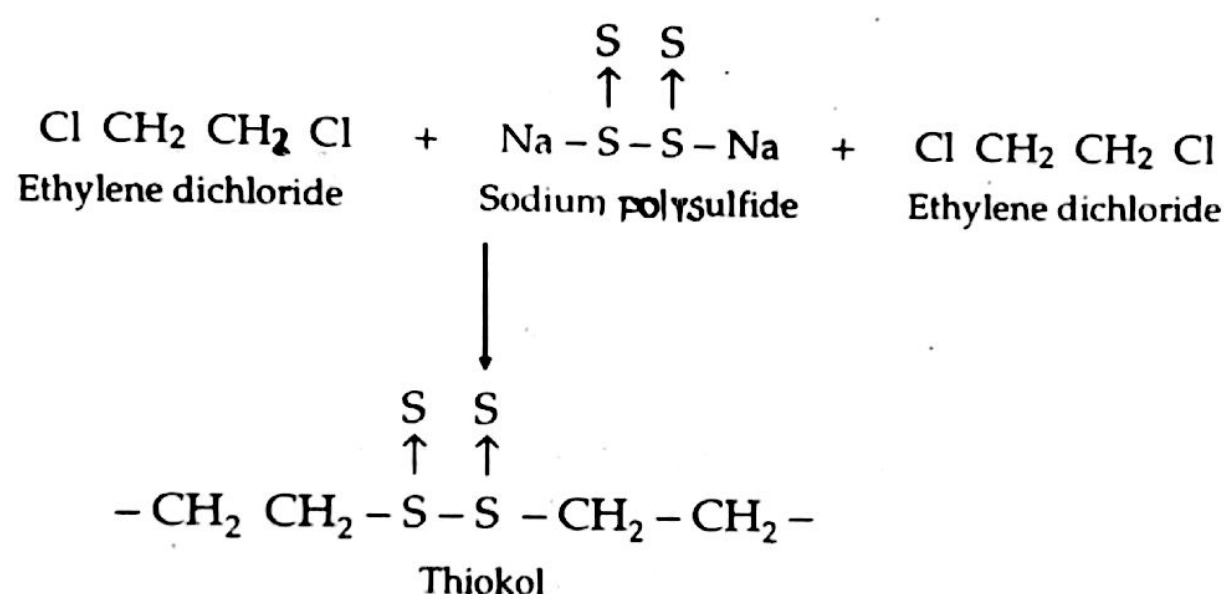
As can be seen from the figure, the trans configuration permits highly regular zig-zags that fit together well ; so Gutta percha is highly crystalline & non-elastic.

Because of all cis-configurations about the double bond, there are only weak van der Waals forces in natural rubber. The double bonds in the rubber molecule are highly important. As they provide reactive allylic hydrogens for vulcanization. The vulcanization process leads to the formation of sulfur bridges between different chains and make the rubber harder & stronger

## 8.2 Polysulphide Rubber (or GR-P or Thiokol)

*Preparation.* It is prepared by the condensation polymerization of sodium polysulphide ( $\text{Na}_2 \text{S}_x$ ) and ethylene dichloride ( $\text{Cl CH}_2 \text{CH}_2 \text{Cl}$ ).

In these elastomers, sulfur forms a part of the polymer chain.



They can be vulcanized by metal oxides such as zinc oxide.

*Properties.* Thiokols have following characteristics :

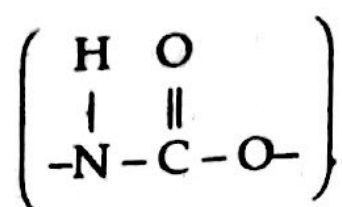
- They have excellent resistance to swelling and disintegration by organic solvents and gasoline, kerosene, lubricating oils.
- Outstanding resistance to oxygen, ozone and sun-light.
- It undergo swelling by benzene and derivatives of benzene.
- It has lower tensile strength and modulus than natural rubber. Under continuous pressure, it tends to lose shape.
- It has offensive-mercaptan-like odour, which restricts its use.

*Applications.* It is used for the

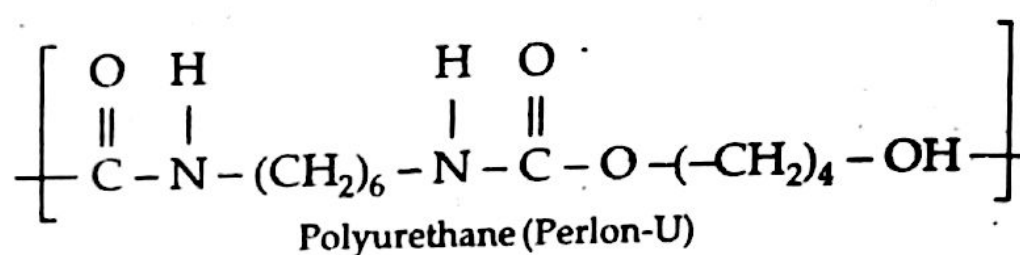
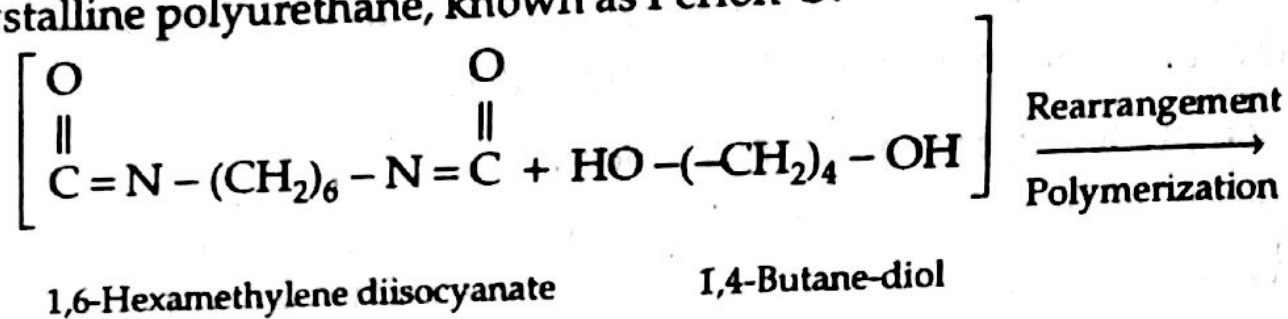
- Manufacture of oil hoses, chemically resistant tubing (for conveying gasoline and oil) and engine gaskets ;
- Diaphragms and seals in contact with solvents ;
- Printing rolls,
- Containers for transporting solvents and
- Solid propellant fuels for rockets, etc.

## 8.3 Polyurethane (PU)

*Preparation.* Polyurethanes are prepared by the rearrangement polymerization of di-(or poly) isocyanate with di-(or poly-) hydric alcohol, and they contain the characteristic urethane linkages,



For example, the reaction of 1, 4 - butane diol with 1, 6 -hexane diisocyanate gives a crystalline polyurethane, known as Perlon-U.



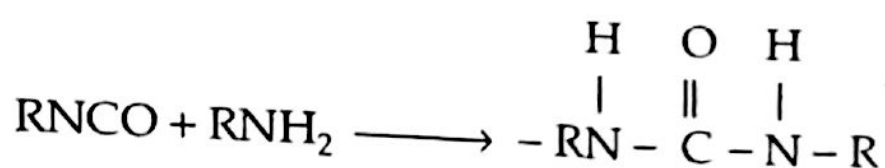
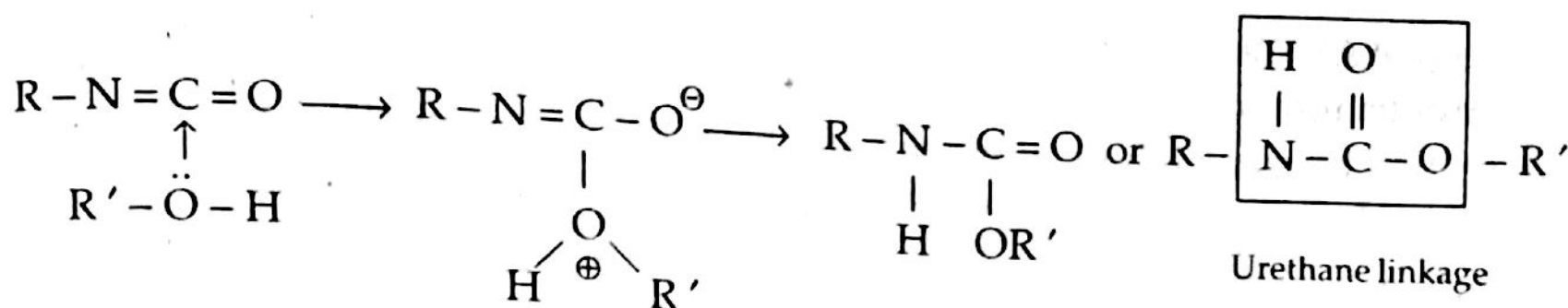
*Properties :*

- (a) Because of their saturated character, they are highly resistant to oxidation ;
- (b) In comparison with Nylons, Polyurethanes are less stable at elevated temperatures ;
- (c) They have good resistance to many organic solvents, but are attacked by concentrated and hot acids and alkalis.
- (d) Suitable choice of diisocyanate and diol and other additives will result in the production of polyurethanes which can be used as coatings, elastomers, fibers and foams. Their properties are summarized below :

Polyurethane Type	Characteristics
(i) Coatings	Resistant to impact, abrasion, greases, oils etc.
(ii) Elastomers	Excellent abrasion resistance, good elasticity and hardness, resistance to oils, greases and solvents.
(iii) Fibers	Resilient PU fibers are very popular as spandex.
(iv) Foams	Both flexible and rigid foams can be prepared which are light, and tough. The foams also have good resistance to weathering, abrasion, heat and chemicals.

- (e) For the formation of foamed polyurethane, little water has to be incorporated, in the reaction mixture of diisocyanate and diol. This is due to the fact that water reacts with isocyanate group to evolve carbon dioxide which foams the polymer as it sets. Amine is also produced and is incorporated into the polymer by its reaction with other isocyanate group.





Polyurethane foams derived from a polyhydric alcohol (which provides large number of hydroxyl groups) are rigid.

Applications :

- Polyurethanes are used for the coatings of gymnasium and dance floors.
- Elastomeric polyurethanes are used for enhancing the life of tyre treads. They are also used for making small industrial wheels and shoe-soles.
- Resilient PU fibers (spandex) are used for making swim-suits and foundation garments.
- Flexible foamed polyurethanes are used for making car and furniture cushions. They are also very good leather substitute and well known in market as cor-foams, used for making pillows, mattresses.

#### 8.4 Styrene Rubber (GR-S or Buna-S or SBR)

**Manufacture.** This rubber is manufactured by copolymerization of butadiene with styrene. *Butadiene* is prepared by passing butane over cupra-ammonium

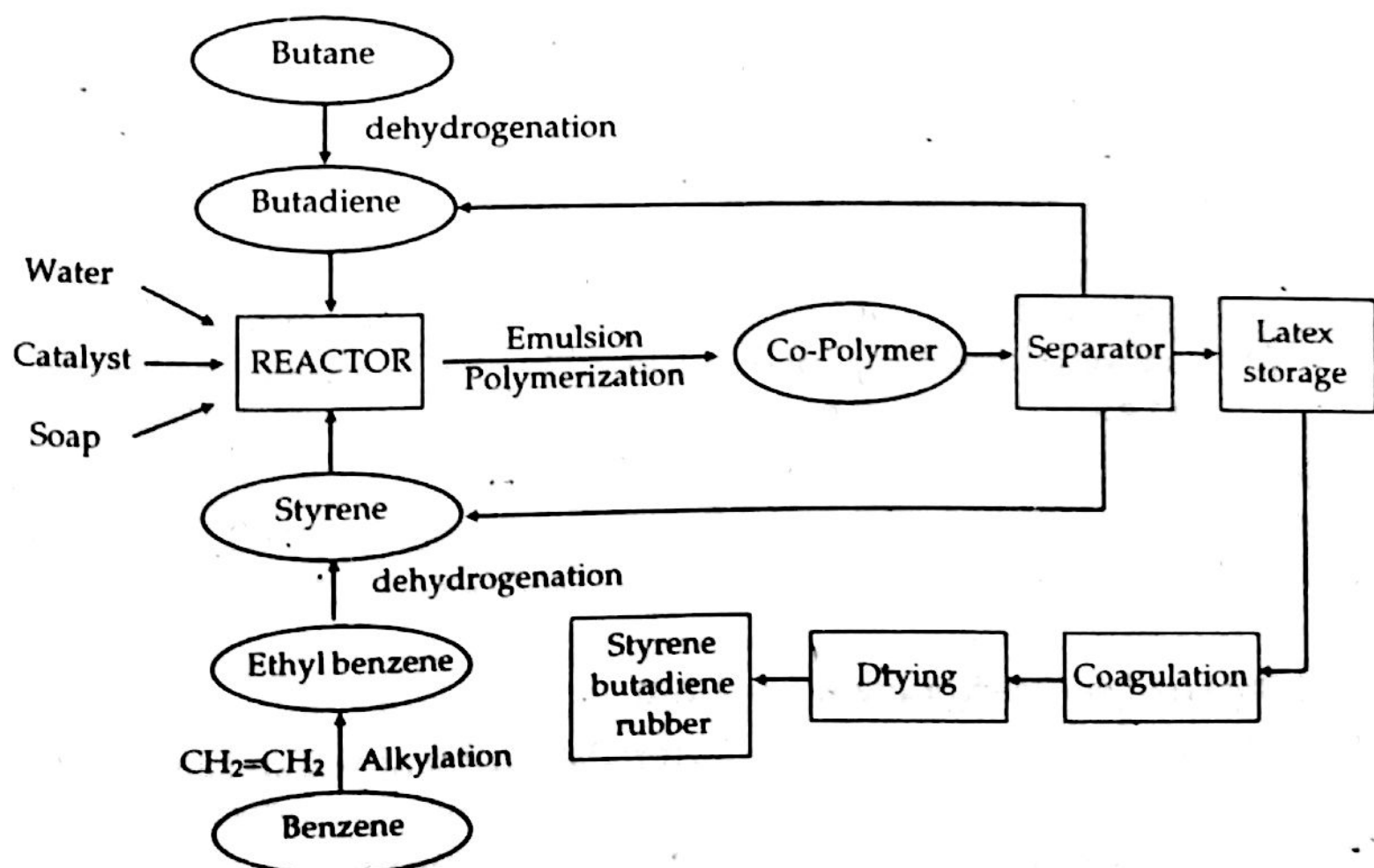
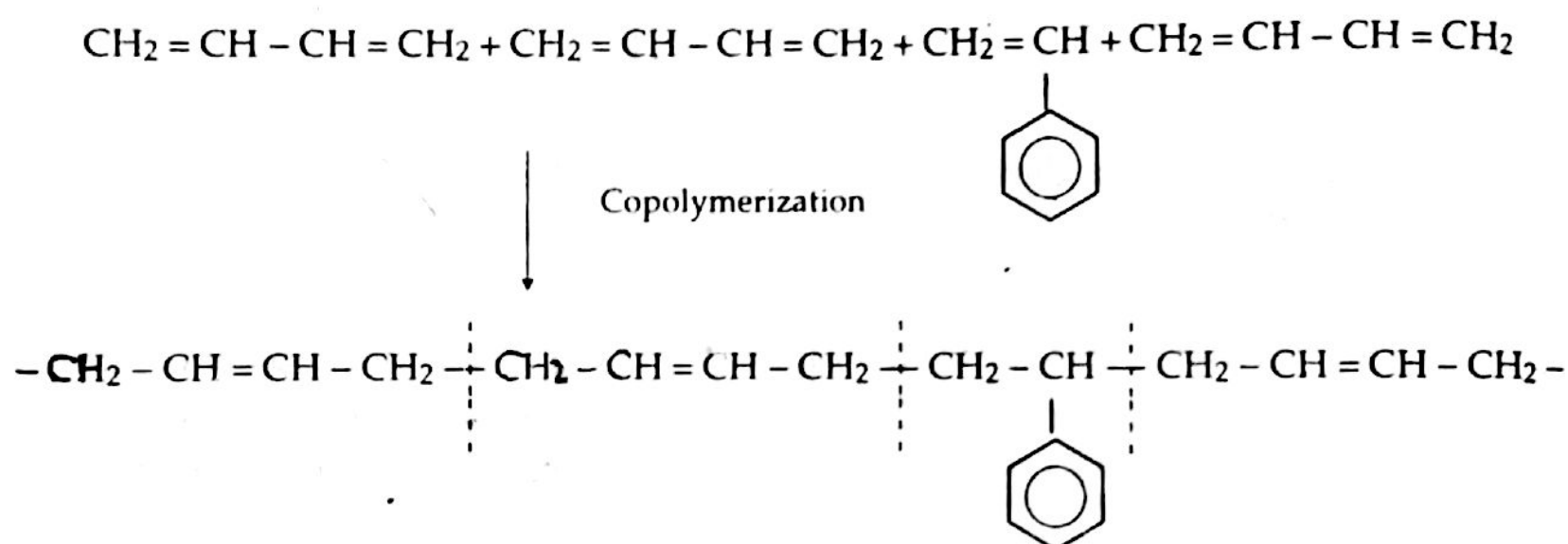


Fig. 8. Simplified flowchart for SBR manufacture.

acetate (CAA) under pressure and at high temperature. Under these conditions, dehydrogenation of butane occurs and butadiene is formed. For the production of styrene, first benzene is alkylated with ethylene so as to get ethyl benzene which is subsequently dehydrogenated over anhydrous aluminium chloride catalyst.

Butadiene (75% by weight) and styrene (25% by weight) are dispersed in water with the help of an emulsifying agent (like soap). Subsequently, emulsion polymerization is started with cumenehydroperoxide initiator. After the completion of polymerization, polymer styrene-butadiene rubber is produced.



If the emulsion polymerisation is carried out at low temperatures ( $-18^\circ$  to  $5^\circ$ ) in the presence of redox catalyst (like cumene hydroperoxide + dextrose) in the presence of iron salt, the resultant SBR is known as *cold rubber*.

Since SBR contains double bonds so vulcanization can be done in the same way as natural rubbers either by sulphur or sulphur monochloride ( $\text{S}_2\text{Cl}_2$ ). Less sulphur and more accelerators are required for vulcanization. Carbon black as reinforcing filler is essential to achieve good physical properties.

**Properties.** SBR has the following characteristics :

- (a) High abrasion resistance,
- (b) High load bearing capacity,
- (c) Resilience,
- (d) It swells in oils and solvents,
- (e) Low oxidation resistance, as it gets readily oxidised, especially in presence of traces of ozone present in the atmosphere.
- (f) Vulcanised and compounded cold rubber has a greater tensile strength and greater abrasion resistance than the SBR or natural rubbers.

**Applications.** SBR is used in following applications :

- (a) Motor tyres ; (b) Shoe Soles ; (c) Foot wear components ; (d) Insulation of wire and cables ; (e) Carpet backing ; (f) Gaskets ; (g) Adhesives and (h) Tank-lining etc.

### 8.5 Nitrile rubber (GR-A or Buna-N or NBR)

**Manufacture.** GR-A rubber is manufactured from butadiene and acrylonitrile. Acrylonitrile is prepared from acetylene and HCN using  $\text{Cu}_2\text{Cl}_2$  as catalyst. Butadiene is prepared from butane by catalytic dehydrogenation.

To prepare Nitrile rubber, butadiene (3 wt. %) and acrylonitrile (1 wt. %) are mixed with water so as to get emulsion which is stabilized by adding soap (emulsifying agent). By this technique of emulsion polymerization, Nitrile rubber is manufactured.

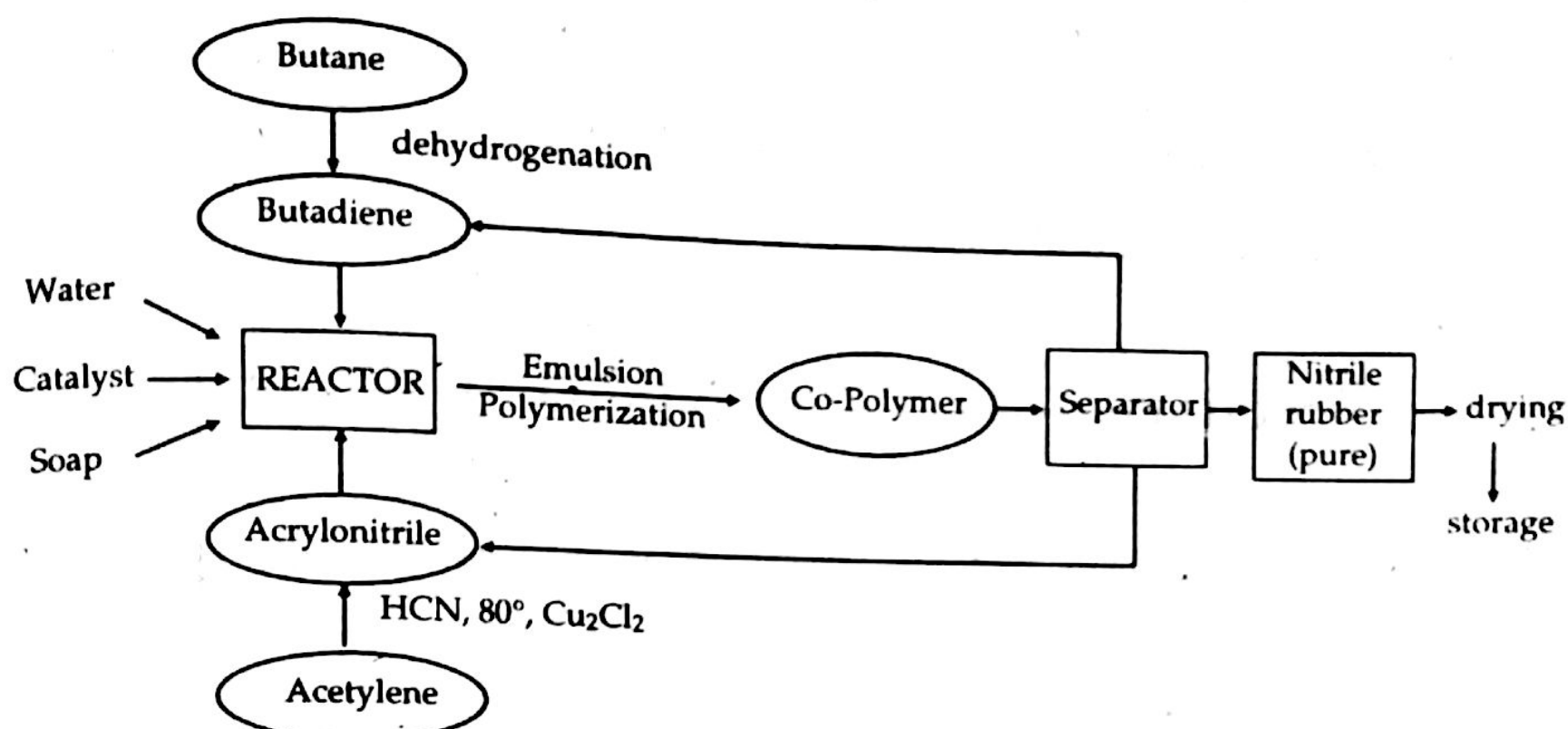
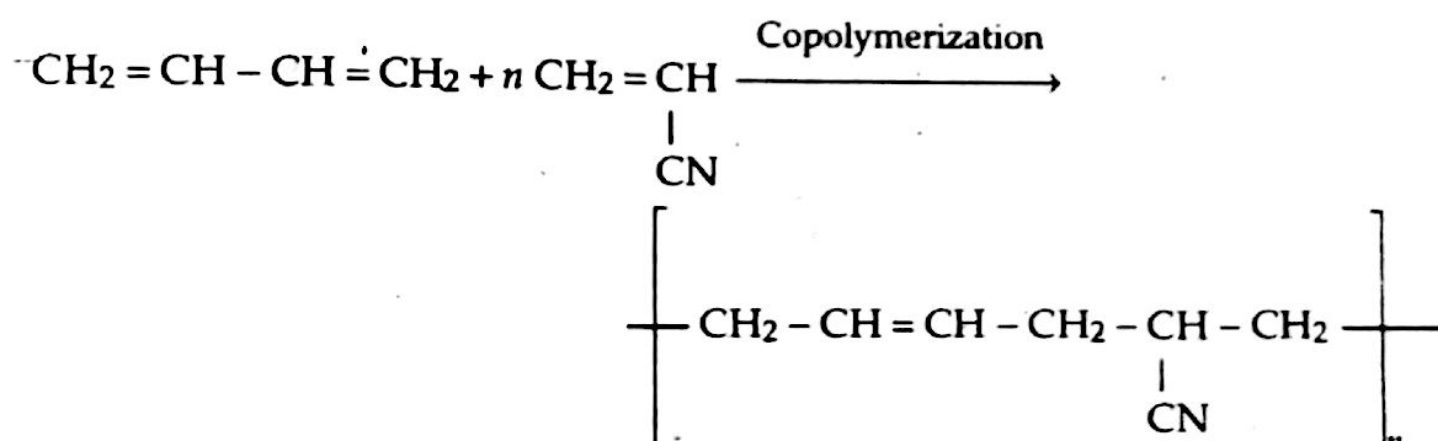


Fig. 9. Simplified flowchart for nitrile rubber manufacture.



Compounding and vulcanisation methods are similar to those of natural rubber.

#### Properties :

- Due to the presence of cyano groups, nitrile rubber is less resistance to alkalis than natural rubber ;
- Excellent resistant to oils, chemicals, aging (sun light). As the acrylonitrile percentage is increased in nitrile rubber, its resistance to acids, salts, oils, solvents etc. increases. But the low temperature-resilience suffers.
- Compared to natural rubber, nitrile rubber (vulcanised) has more heat resistance and it may be exposed to high temperatures.
- It has good abrasion resistance, even after immersion in gasoline or oils.

**Applications.** Nitrile rubber is used for  
 (a) Conveyor belts ; (b) Lining of tanks ; (c) Gaskets ; (d) Printing rollers ;  
 (e) oil-resistance foams ; (f) Automobile parts and high altitude air-craft components, (g) Hoses and (h) Adhesives.



### 8.6 Neoprene (GR-M)

Neoprene is a polymer of chloroprene and is therefore also known as *polychloroprene*. Chloroprene is 2-chloro-1-3-Butadiene. Catalytic dimerization of acetylene results in the formation of vinyl acetylene which reacts with HCl in presence of aqueous cupra ammonium chloride to give chloroprene. Chloroprene undergoes emulsion polymerisation to give neoprene.

The involved chemical reactions are :

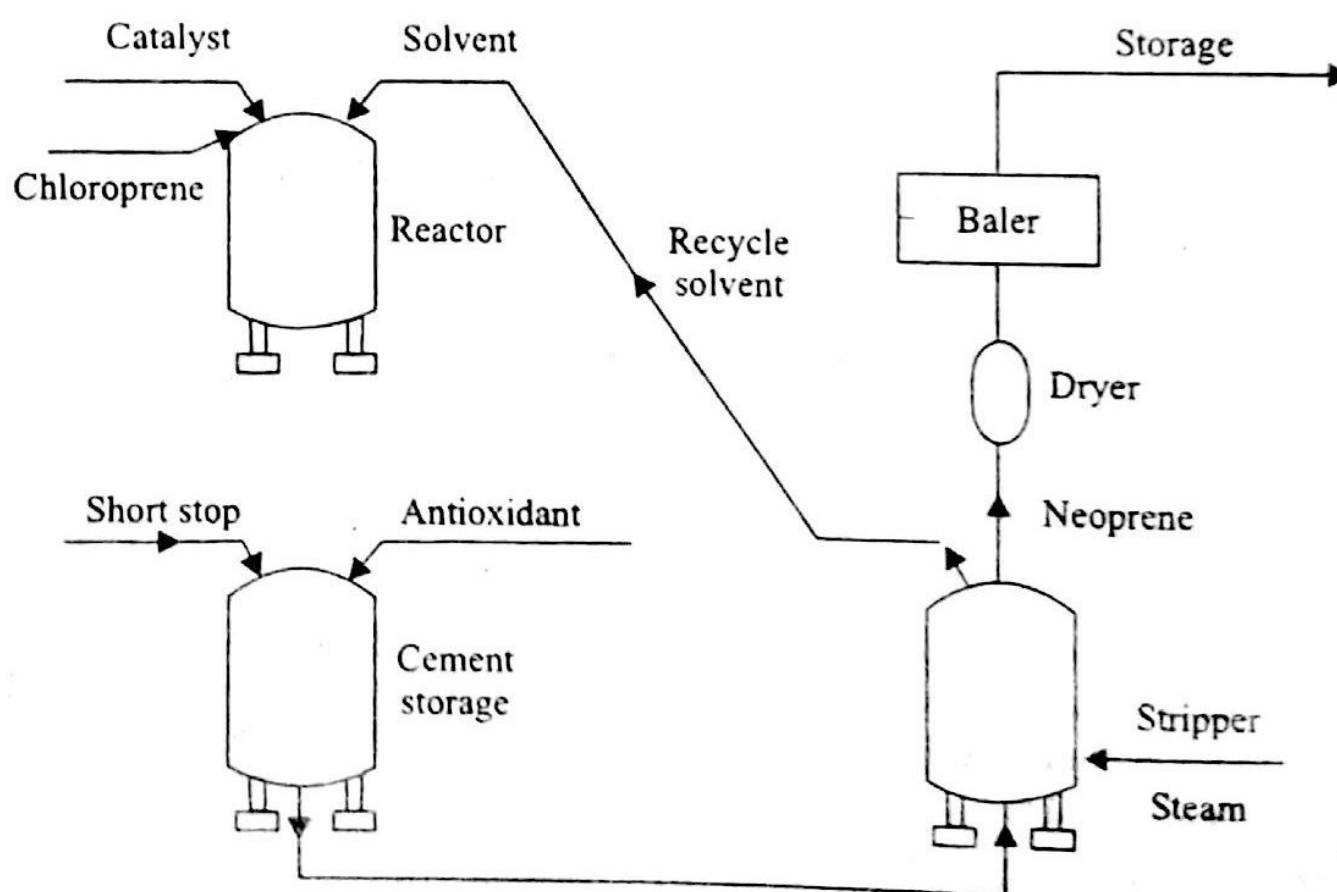
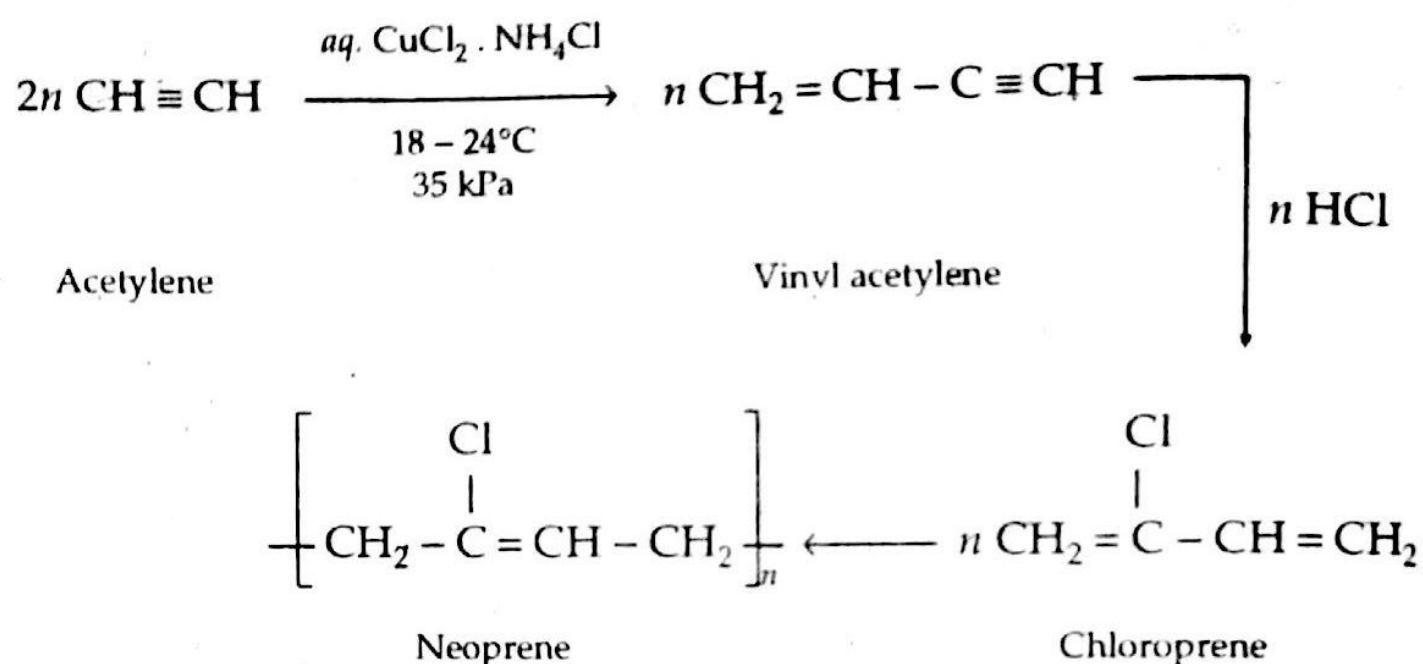


Fig. 10. Flowsheet for Neoprene.

*Properties.* Neoprene has the following properties :

- The presence of chlorine and trans-linkages impart superior resistance to vegetable and minerals oils, and high temperature,
- Being polar polymer, it has greater solubility in polar solvents.

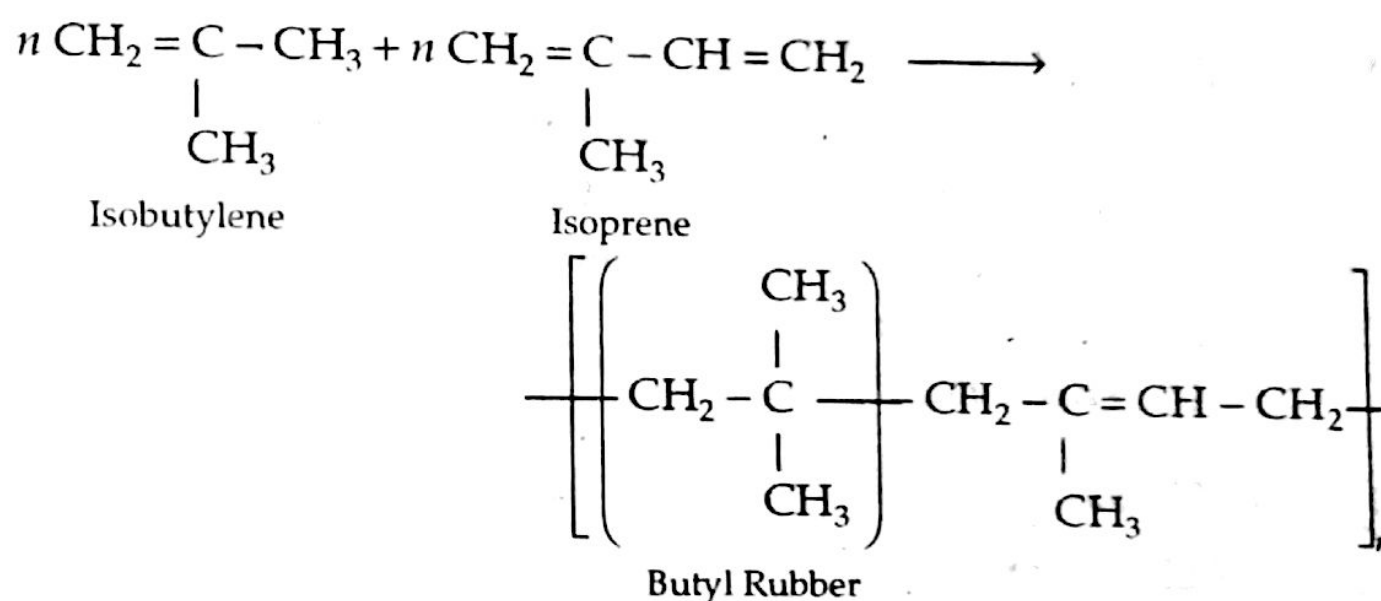
- (c) It has high tensile strength even in the absence of carbon black.
- (d) It does not undergo oxidative degradation easily because of its good ozone and weathering resistance.
- (e) Resistance to oils is superior than natural rubber but poor than nitrile rubber.

*Applications.* Neoprene is used for

- (a) Wire and cable insulation ;
- (b) Gloves ;
- (c) Industrial hoses and Gaskets ;
- (d) Tubing for carrying corrosive gases and oils ;
- (e) Lining of reaction vessels,
- (f) conveyor belts,
- (g) Adhesives and
- (h) Shoe-soles.

### 8.7 Butyl Rubber (GR-I)

Butyl rubber is also known as polyisobutylene because it is a copolymer of isobutylene (95 – 99%), with small amount of isoprene (1 – 5%), for its easy vulcanization.



**Manufacture.** The butyl rubber is manufactured by polymerizing isobutylene with isoprene in methyl chloride solvent. The mixture is fed to stirred reactor. Anhydrous  $\text{AlCl}_3$  in methyl chloride acts as a catalyst for polymerization.

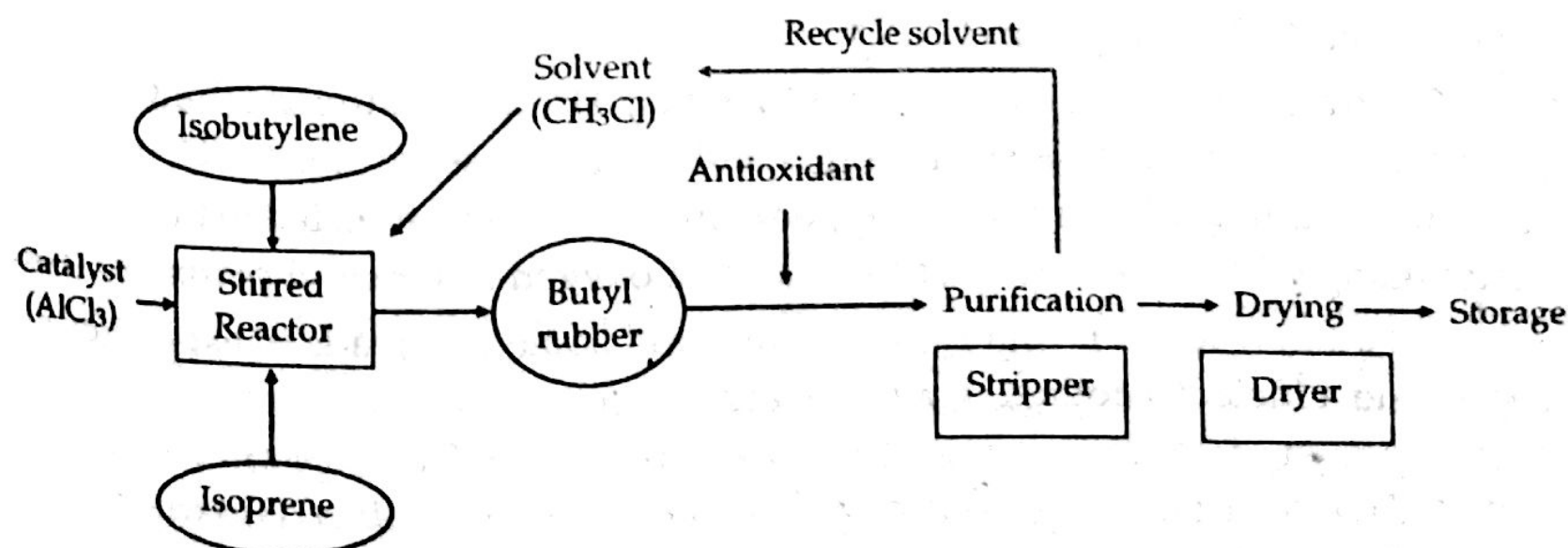


Fig. 11. Simplified flowsheet for Butyl Rubber manufacture.

**Properties.** Butyl rubber has following characteristics :

- (a) Under normal conditions it is amorphous but it crystallizes on stretching ;
- (b) It is quite resistant to oxidation due to low degree of unsaturation ;
- (c) Due to very low unsaturation, it can be vulcanized but it cannot be hardened much.
- (d) It can be degraded by heat or light to sticky low-molecular weight products so stabilization (by usual rubber antioxidants or free radical reaction retarders) is must.
- (e) Because of its hydrocarbon nature, butyl rubber is soluble in hydrocarbon solvents like benzene but has excellent resistance to polar solvents like alcohol, acetone and ageing chemicals (e.g., HCl, HF, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> etc.)
- (f) Being non-polar, it has good electrical insulation properties,
- (g) Compared to natural rubber it possesses outstanding low (About 1/10<sup>th</sup>) permeability to air and other gases.
- (h) It does not crystallize on cooling and hence remains flexible down to - 50 °C.

**Application.** It is used for

- (a) Insulation of high voltage wires and cables ;
- (b) Inner tubes of automobile tyres ;
- (c) Conveyor belts for food and other materials ;
- (d) Lining of tanks ;
- (e) Hoses etc.

## 9 PLASTICS

### 9.1 Polyethylene

It is also known as polythene. It is prepared by the process of addition polymerization of ethylene ( $\text{CH}_2 = \text{CH}_2$ ). There are following types of polyethylene :

#### (i) Low Density Polyethylene (LDPE)

**Manufacture of Low density polythene by High pressure method.** In this method, purified ethylene is first liquified under high pressure (1000 – 3000 atmosphere) with the help of primary and hyper-compressors. It is then fed to the tubular reactor along with catalyst (like  $\text{H}_2\text{O}_2$ , traces of oxygen or benzoyl peroxide). The polymerization reaction is highly exothermic and sometime leads to explosion, so proper and efficient cooling is a must and is done via. cooling towers. After polymerization, reaction mixture is carefully transferred to separator in which unreacted ethylene is removed and recycled. The polymer obtained is extruded and pelletized. After drying, polyethylene pellets are stored. .



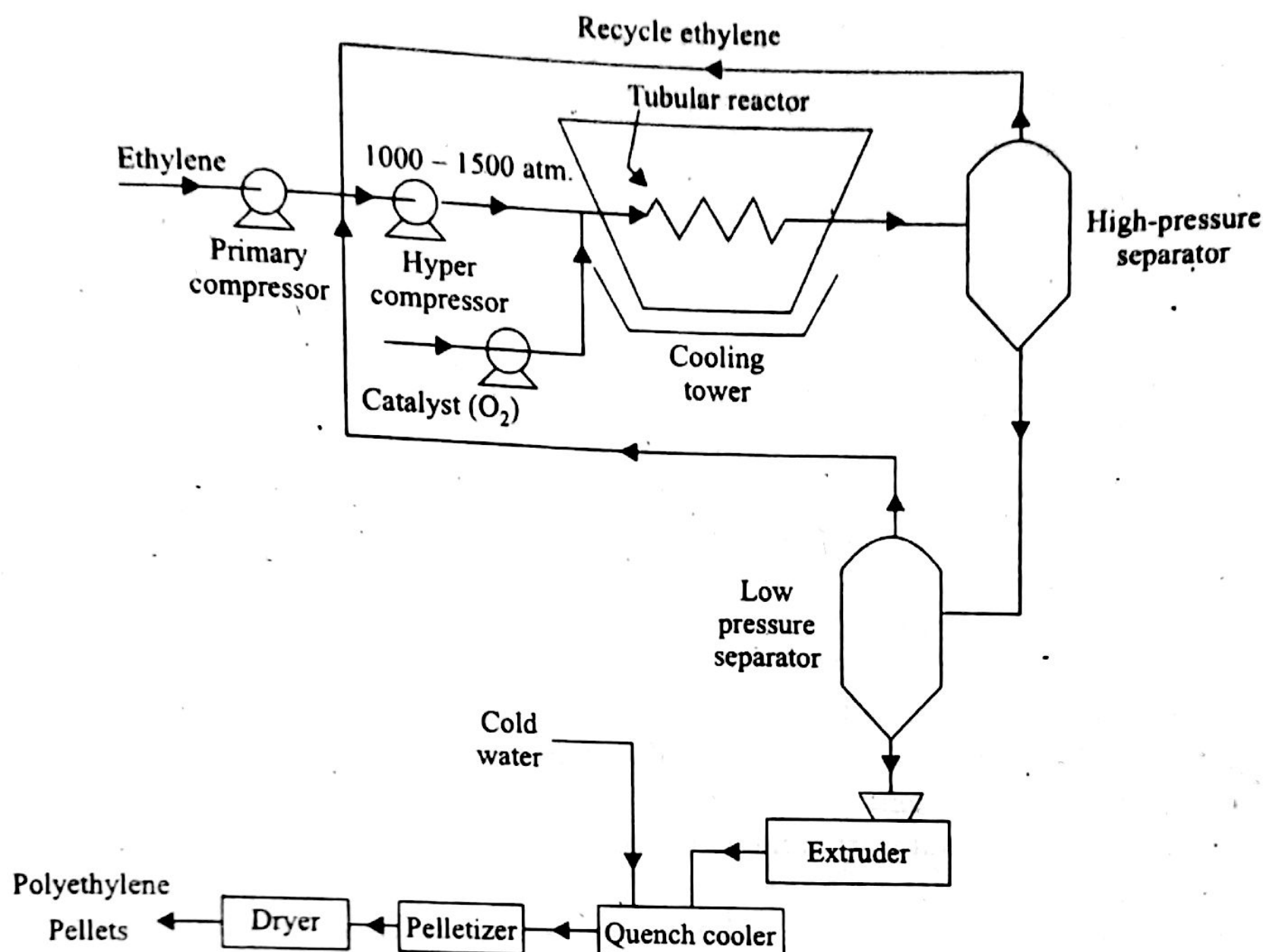


Fig. 12. Flow diagram for production of Low-density Polyethylene by High-pressure method.

*Properties :* (a) During the propagation steps, large number of chain transfer reactions results in the formation of branched structures. These branches are mainly short chain and occasionally long chain. These branches do not allow the molecules to pack efficiently and hence its density is low.

Density is about  $(0.91 - 0.925 \text{ gm/cm}^3)$ .

(b) Due to the same reasons, crystallinity of LDPE is also low ( $\sim 55\%$ ).

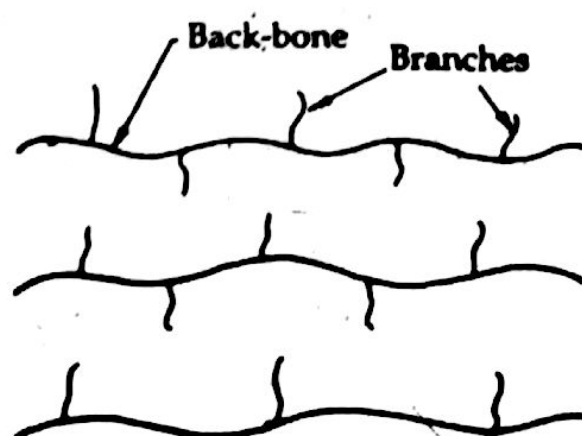


Fig. 13. Structure of LDPE.

(c) As it is non-polar polymer so there are no strong intermolecular forces. Moreover, the backbone is flexible. Both these factors are responsible for low softening temperature of LDPE, which is only  $115^\circ \text{C}$ .

(d) LDPE is chemically inert and has excellent chemical resistance.

(e) As it is non-polar, hence it has excellent electrical insulation properties.

(f) It is tough and flexible even at low temperatures.

**Applications.** LDPE is used in following applications :

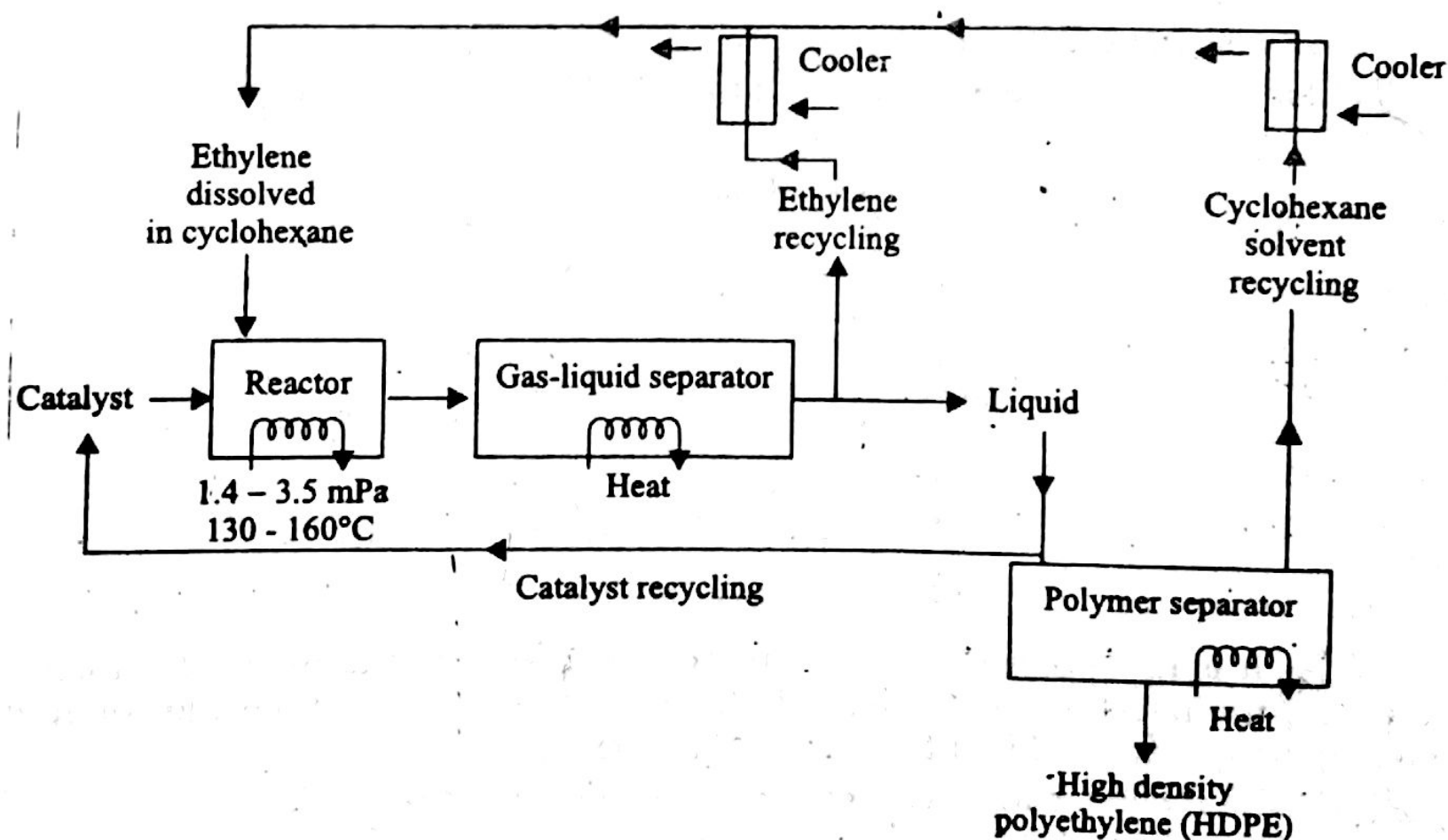
- (a) Films for general packaging and carrier bags ;
- (b) squeeze bottles particularly for detergents ;
- (c) Moulded toys ;
- (d) Ink tubes for pens and
- (e) Mugs.

**Limitations of LDPE**

- (a) Because of low density and % crystallinity, LDPE has low rigidity and is not suitable for load bearing applications. For instance, if pipes are made from LDPE for domestic water, they will undergo creep.
- (b) LDPE is permeable to gas molecules because in the amorphous zones the free volume and segmental movements facilitate the passage of small molecules. Hence, LDPE is also not suitable for the manufacture of pipes for distribution of gas.

**(ii) High density polyethylene (HDPE)**

**Manufacture of High density polythene by Low pressure method.** In the **phillips process**, ethylene (dissolved in a liquid hydrocarbon such as cyclohexane) is polymerised by a supported metal oxide catalyst (5% of  $\text{CrO}_3$  on a finely divided silica-alumina catalyst, activated by heating to about  $250^\circ\text{C}$ ) at 1.4 – 3.5 MPa pressure and at about  $130 - 160^\circ\text{C}$ . The inert solvent serves to dissolve polymer as it is formed and as a heat transfer medium. After reaction the mixture is passed to a gas-liquid separator where the ethylene is flashed off, catalyst is then removed from the liquid product of the separator and the polymer separated from the solvent by either flashing off the solvent or by precipitating the polymer by cooling. Polyethylenes of highest density ( $\sim 0.96 \text{ g/cm}^3$ ) can be obtained by this process.



**Fig. 14.** Simplified flowsheet for HDPE manufacture.

*Properties :*

- (a) The HDPE molecules are linear and their packing is easy. Hence HDPE has high density (0.95 – 0.97) and more percentage crystallinity (80 – 90%).
- (b) Softening temperature of HDPE (135° C) is also higher, compared to LDPE.
- (c) HDPE has excellent chemical resistance.
- (d) It has excellent electrical insulation properties.
- (e) Because of lower number of amorphous zones, HDPE has sufficiently low water and gas permeability.
- (f) It is free from odour and toxicity.
- (g) It is more stiff, hard and possesses greater tensile strength compared to LDPE.



Fig. 15. Structure of HDPE.

*Applications :*

- (a) Because of crisp feel and greaseproof nature, HDPE film is used as wrapping material instead of paper for food products.
- (b) Because of better oxidation and UV-resistance, HDPE is used for the manufacture of crates, food tubs, Industrial containers and overhead tanks.
- (c) It can also be used for domestic water and gas piping.
- (d) Bottles for milk, household chemicals and drug packaging are also made from it.

**9.2 Polyvinyl chloride (PVC)**

PVC is made by addition polymerization and is of following *two* types :

**(i) Rigid PVC**

**Manufacture.** PVC can be made from vinyl chloride by bulk, suspension and emulsion polymerisation. Here we will discuss only the emulsion polymerisation. Because of its low water-solubility (0.09% at 20°C) vinyl chloride may be polymerised in emulsion. Using secondary alkyl sulphonates or alkali salts of alkyl sulphates as emulsifiers rapid polymerization can occur in oxygen-free environments. Generally, water soluble initiators like ammonium persulphate,  $H_2O_2$  etc.

For polymerisation of vinyl chloride, it is mixed with water in equal parts, small amount of catalyst and an emulsifier. The mixture is vigorously stirred and then sent to autoclave at temperature of 40 – 45°C. The polymerization is completed in 60 – 70 hours. The polymer is coagulated by acid and dried. The desired properties in PVC can be achieved by using plasticizers, stabilizers, lubricants and fillers.



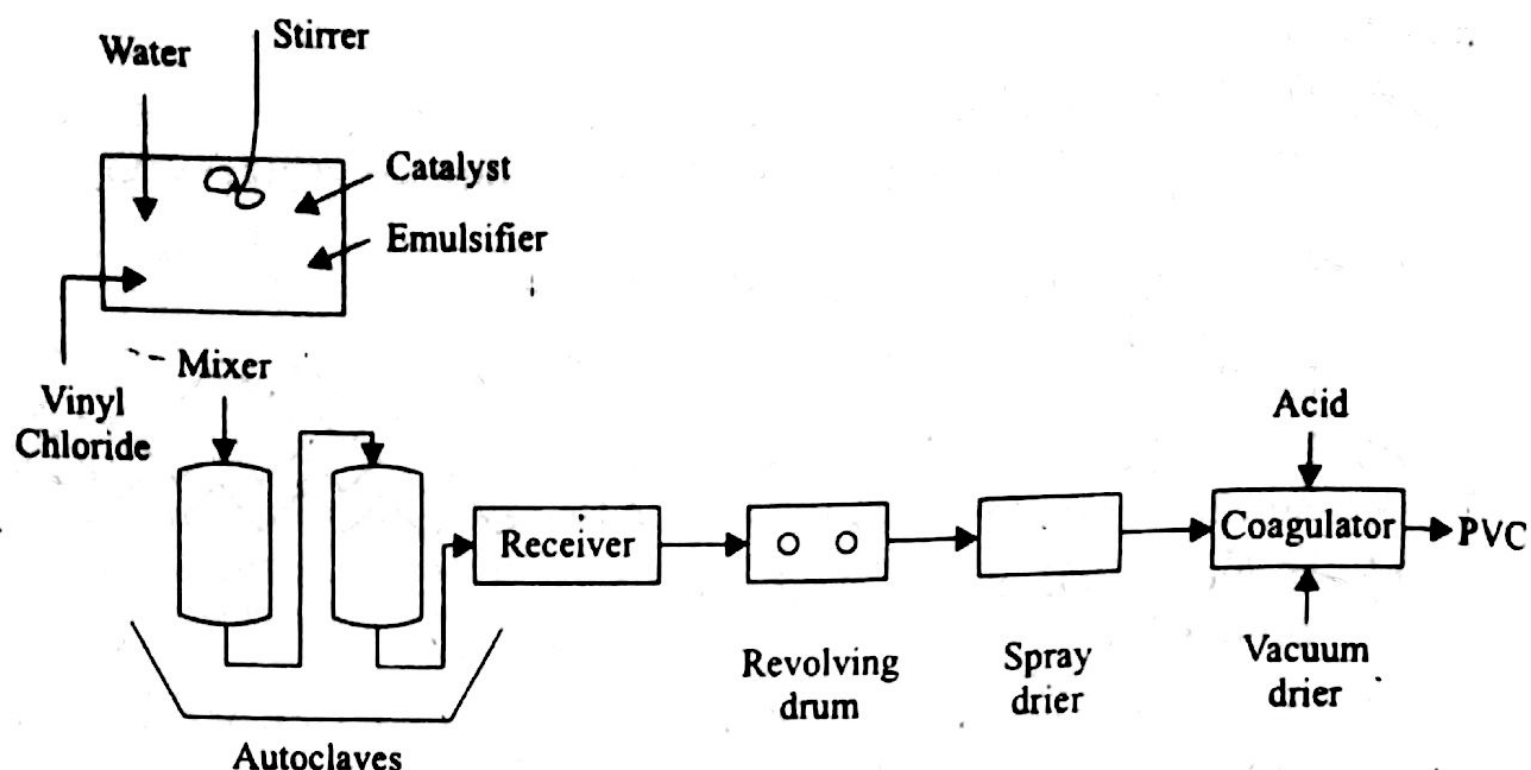
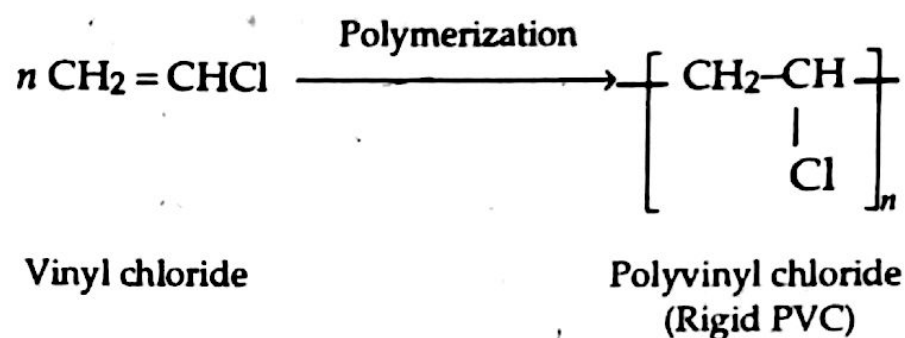


Fig. 16. Flowsheet for manufacture of PVC.



**Properties.** The PVC obtained above is known as rigid PVC or unplasticized PVC and has the following properties :

- (a) Presence of chlorine atoms on the alternate carbon atoms of PVC causes an increase in the interchange attraction. This increases the hardness and stiffness of polymer. its softening point is also high ( $148^\circ \text{C}$ ).
- (b) The C-Cl dipole makes PVC a polymeric polar molecule, but because of the immobility of the dipole at room temperature (since  $T_g(\text{PVC}) = +80^\circ \text{C}$ ), power factor of PVC is comparatively low.
- (c) PVC is colourless, odourless and non-inflammable.
- (d) It has superior chemical resistance but is soluble in ethyl chloride and tetrahydrofuran.
- (e) It has excellent oil resistance and resistance to weathering.

**Applications of rigid PVC :**

- (a) It is used in acid recovery plants and in plants for handling hydrocarbons, many of which adversely affect the polyolefins. This is due to its very good resistance to chemicals.
- (b) Rigid PVC has great potential importance to building industry since it has excellent resistance to weathering. When considered regarding initial cost, Installation and maintenance cost, it is found to be very economical. Hence, it is used for making pipes for drainage and Guttering. Moreover, it is also replacing wood for making window frames that neither corrode nor rot.

(c) It is also used for making bottles :

- (i) for consumable liquids (like Edible oils, fruit squashes, table wine and vinegar).
- (ii) for liquids of household use (like bisleri mineral water, cosmetics and detergents).

In this application, compared to glass, PVC is less brittle, lighter, has greater design flexibility, better clarity, oil-resistance and barrier properties.

### (ii) Plasticized PVC

*Preparation.* It is obtained by adding plasticizers such as DOP (dioctyl phthalate), dibutyl phthalate, tricresyl phosphate etc. to rigid PVC.

*Properties and applications of plasticised PVC :* (a) Plasticised PVC is very good insulator for direct current and low frequency AC current. it has completely replaced rubber insulated wire for domestic flex and is used widely industrially. It is also used for sheathing in cables where PE, is employed as insulators.

(b) Plasticized PVC is used for making leather cloth which is used in

- (i) Car applications in upholstery and trim ;
- (ii) Kitchen upholstery ;
- (iii) Bathroom curtaining and
- (iv) Ladies handbags.

compared to leather, PVC-leather cloth has greater abrasion resistance, flex resistance and washability. Moreover, its cost is low.

(c) It is also used for making

- (i) Plastic rain wear ;
- (ii) Baby-pants ;
- (iii) All PVC-shoes for beach wear and
- (iv) Garden hose.

These applications are due to flexibility and water-proof nature of plasticized PVC. It is also more economical and better aesthetically.

### 9.3 Polyvinyl Acetate (PVA)

**Manufacture.** First vinyl acetate is prepared by vapour phase process. In this process, acetylene is mixed with acetic acid at  $200^{\circ}\text{C}$  in a stainless steel vessel. Then this mixture is passed through vertical reactor tubes which are filled with zinc salt or activated carbon catalyst. The unused acetic acid is recovered by distillation and recycled along with acetylene. Vinyl acetate is purified by distillation and then stabilised of adding hydroquinone inhibitor.

Polyvinyl acetate is prepared by introducing a benzene solution of vinyl acetate mixed with benzoyl peroxide or acetyl chloride as catalyst into a jacketed vessel, maintained at  $72^{\circ}\text{C}$ . After 5 hours heating, the molten resin is taken out into the separator. The solvent and unchanged vinyl acetate are recovered by steam-distillation and then they are recycled.

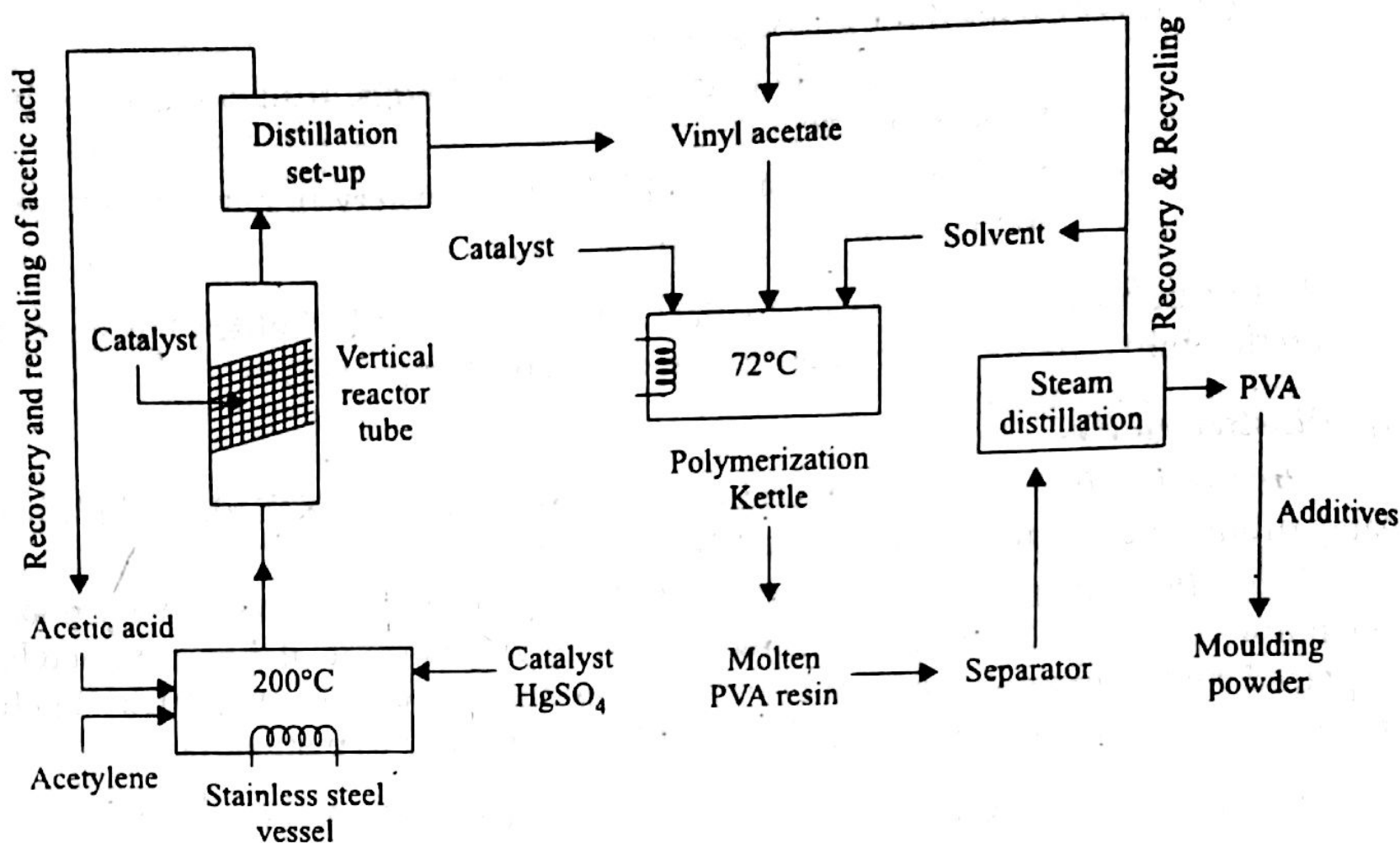
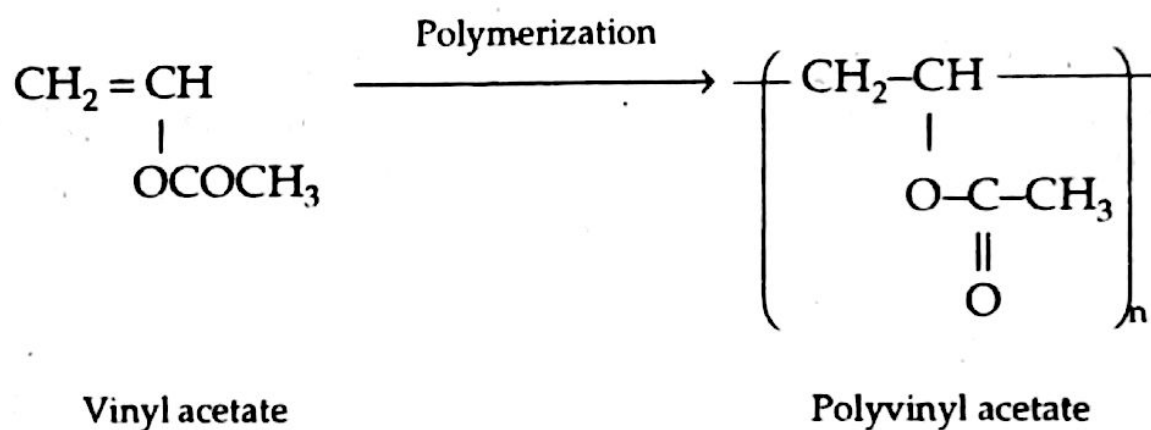


Fig. 17. Simplified flow-sheet diagram for the manufacture of PVA.



**Properties :**

- (i) It is clear, colourless and transparent material,
- (ii) It is amorphous polymer and has low  $T_g$  (only  $28^\circ \text{C}$ ). Hence, the articles formed from it are distorted even at room temperature under the influence of compressive and tensile forces.
- (iii) Lower molecular weight polymers become gum-like when masticated and hence are used for making chewing gums. Since it is harmless, when taken orally.
- (iv) It is fairly soluble in organic solvents.

**Applications.** It is used for

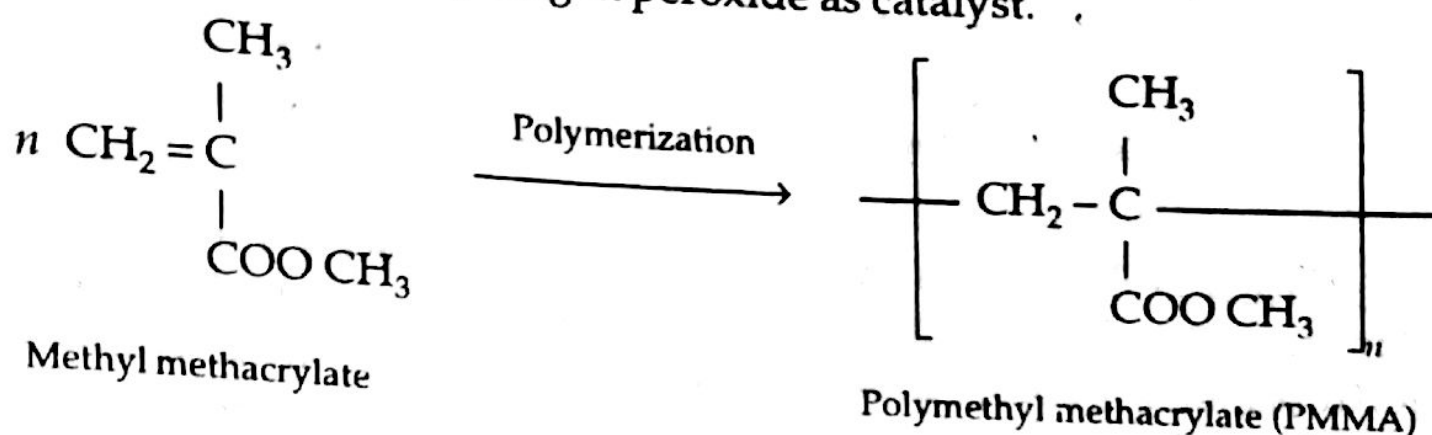
- (a) The production of water-based emulsion paints ;
- (b) making chewing gums ;
- (c) making records,
- (d) Finishing textiles and other fabrics and
- (e) Bonding : Paper, leather, textiles etc.



### 9.4 Polyacrylates

PMMA is also known as plexiglass or Lucite.

*Preparation.* It is prepared by the polymerization of methyl methacrylate in the presence of acetyl peroxide or hydrogen peroxide as catalyst.



*Properties :*

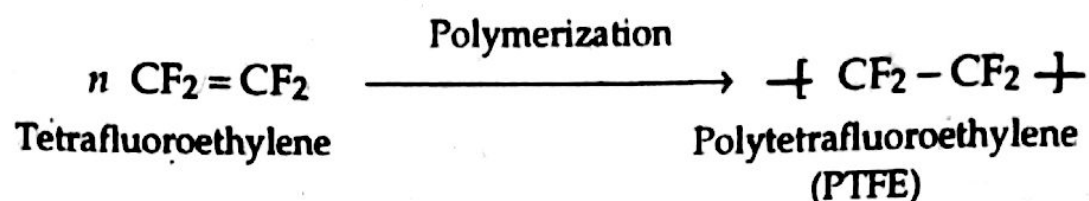
- (a) It is amorphous, colourless, transparent thermoplastic with high optical transparency.
- (b) Methyl groups as substituents on the  $\alpha$ -carbon atoms restrict chain flexibility. That's why PMMA is hard and has significantly higher  $T_g$  (above  $65^\circ \text{C}$ ).
- (c) As it is a polar polymer, hence it does not have electrical insulation properties comparable with polyethylene.
- (d) It has high softening point (about  $130 - 140^\circ \text{C}$ ) due to presence of intermolecular dipole forces which act through the polar groups.
- (e) The interesting property of total internal reflection may be conveniently exploited in PMMA because the critical angle for the polymer-air boundary is  $42^\circ$ . A wide light beam may be transmitted through long lengths of solid polymer.
- (f) Compared to glass, PMMA weighs only one-third, can be readily molded to any desired shape. Moreover, the scratches on it can be easily removed by rubbing it with a cloth moistened with acetone. Compared to PS, PMMA is more tougher. After cracking, fragments formed are less sharp, and less harmful.

*Applications :* PMMA is used for making

- (a) Display signs both illuminated and non-illuminated for internal and external use.
- (b) Light fittings for street lamp housing, ceiling lighting for school rooms, railway stations, factories and offices, and automobile rear lamp housing.
- (c) familiar 'bubble' body of many helicopters.
- (d) Motor-cycle windscreen.
- (e) Wash basins.
- (f) Dome-shaped covers of solar collectors (i.e., solar heaters) and
- (g) Optical fibers.

### 9.5 Polytetra fluoroethylene (PTFE) or Teflon

**Preparation.** Teflon is prepared by the polymerisation of tetrafluoro ethylene under pressure in the presence of benzoyl peroxide as catalyst.



**Properties.** Teflon has twisted zigzag structure with fluorine atoms packing tightly in a spiral around the carbon-carbon skeleton. Due to the presence of highly electronegative fluorine atoms, there are very strong attractive forces between different chains. These strong attractive forces are responsible for its

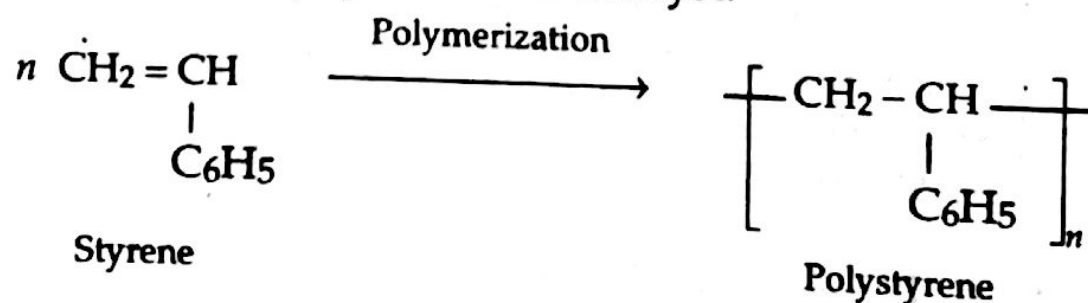
- (a) High density (2.1 to 2.3 gm/cm<sup>3</sup>).
- (b) Chemical inertness over a wide temperature range ;
- (c) Excellent electrical insulation properties ;
- (d) Non-adhesive characteristics ;
- (e) Very low coefficient of friction and
- (f) Excellent toughness and heat resistance.

As it is dense, chemically inert and high temperature softening so teflon behaves somewhat like a thermosetting polymer.

**Applications :** PTFE (Teflon) is used for (a) Wire and cable insulation ; (b) Laminates for printed circuitry ; (c) Coatings of frying pans ; (d) Non-lubricating bearings ; (e) Variety of seals, gaskets, packings valve and pump parts and stop-cocks for burettes and (f) Insulators for motors, generators, coil transformers and capacitors.

### 9.6 Polystyrene (PS)

**Preparation.** Polystyrene is prepared by free radical addition polymerisation of styrene in the presence of benzoyl peroxide as catalyst.



**Properties :**

- (a) Because of the presence of bulky phenyl groups, packing of PS chains is not efficient and hence it is amorphous polymer. Its specific gravity (1.054) is also low.
- (b) It has good optical properties like it is transparent polymer allowing high transmission of all wavelengths. Moreover, its high refractive index (1.592) gives it a particularly high 'brilliance'.
- (c) Due to chain stiffening effect of benzene ring, PS is hard but brittle. It emits a characteristic metallic sound when dropped.
- (d) Being non-polar amorphous polymer, its softening temperature (82 – 100 °C) is low. It cannot withstand the temperature of boiling water.

- (e) As it is non-polar so it has low tendency for moisture absorption. Moreover, it has good electrical insulation characteristics.
- (f) It has reasonable chemical resistance but mediocre oil resistance.

**Applications :** Polystyrene is used for making : (a) Audio cassettes ; (b) Containers for talcum powder ; (c) Housewares (small jars and storage containers) ; (d) Bottle caps ; (e) Combs and (f) Brush handles.

### 9.7 Phenolic Resins

These resins are generally based on *phenol* since they give products with the greatest mechanical strength and speed of cure, but *cresols* may be used in acid-resisting compounds and *phenol-cresol mixtures* in cheaper compositions.

In the manufacture of *novolaks*, stainless steel reaction kettle is used (Refer Fig. 18). A typical charge composition in it can be :

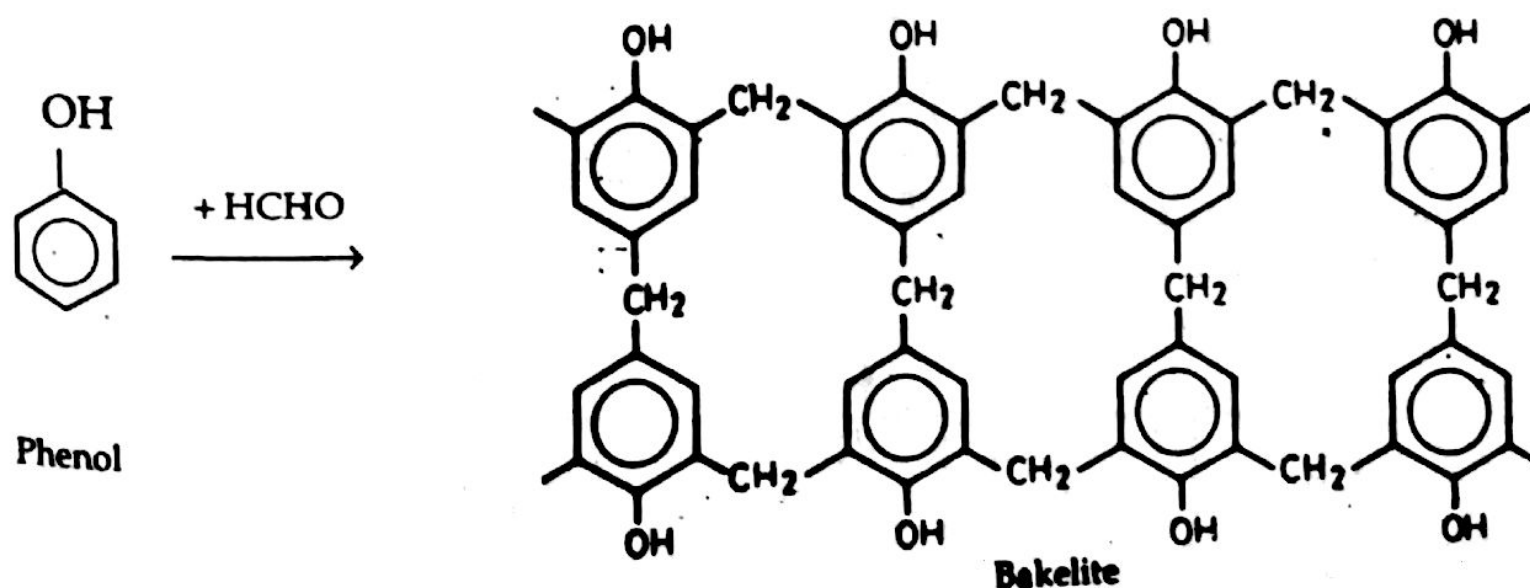
Phenol	100 parts by weight
Formalin (37% w/w)	70 parts by weight
Sulphuric or oxalic acid	1.5 parts by weight

The reaction mixture is heated and allowed to reflux, under atmospheric pressure at about 100°C. The condensation reaction will take 2 – 4 hours then water present is distilled off. A vacuum may be employed for the removal of volatiles present.

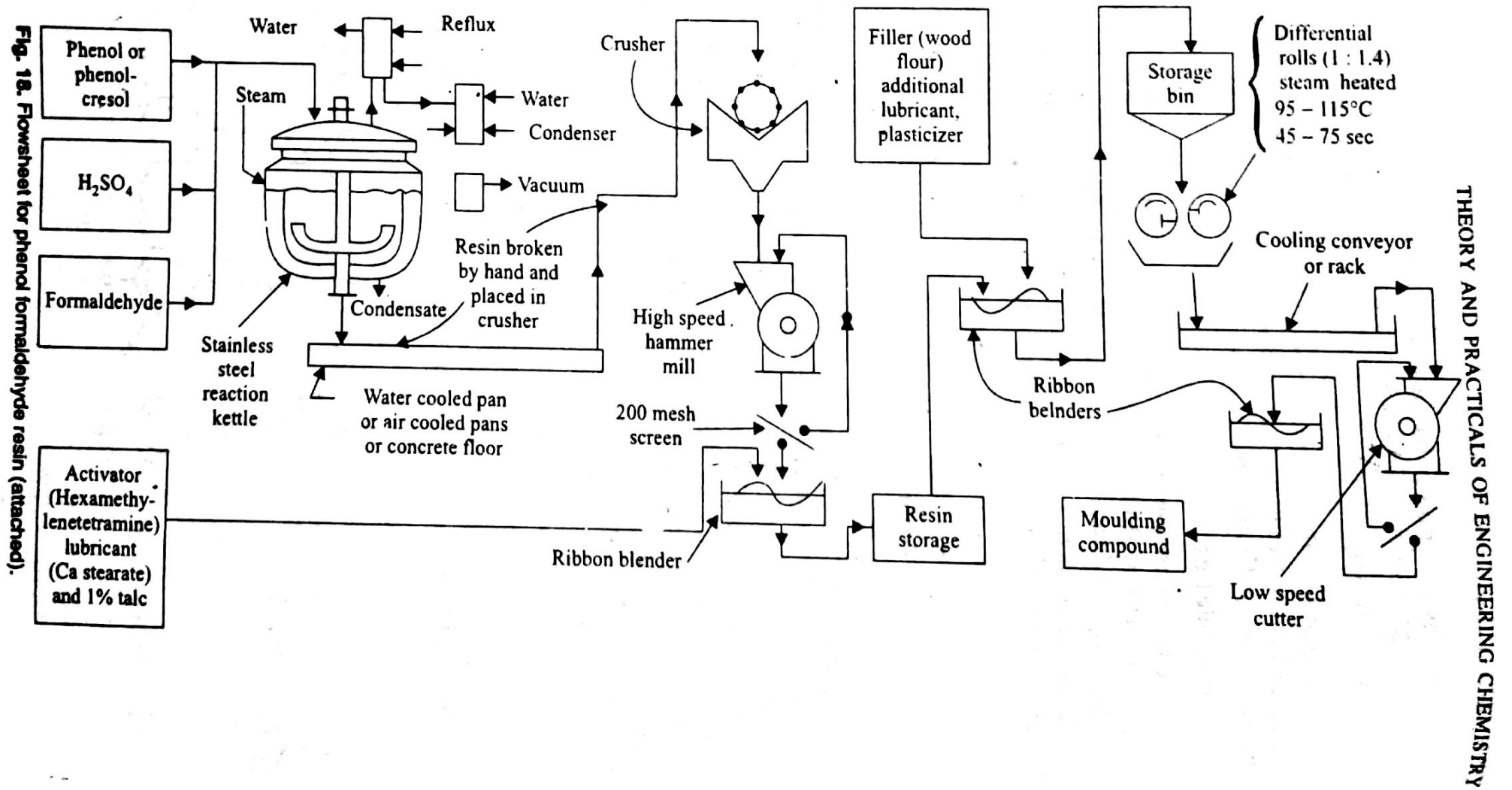
The novolaks are hardened by addition of hexamethylenetetramine (hexaminê, hexa). Because of the exothermic reaction on hardening (cure) and the accompanying shrinkage, it is necessary to incorporate inert materials (fillers) to reduce the resin content. Fillers also improve the shock resistance. Other ingredients may be added :

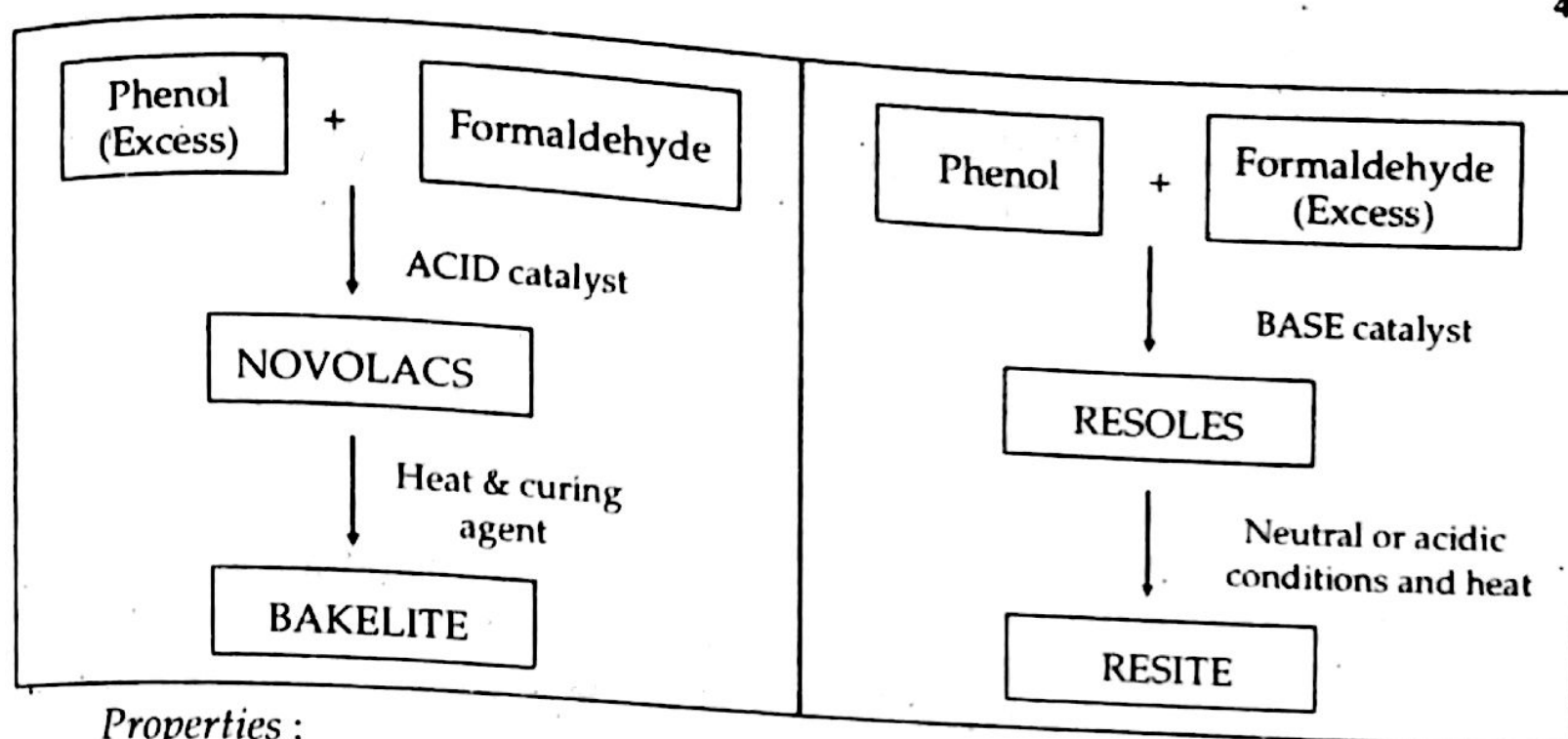
- to prevent sticking to moulds (*lubricants*),
- to promote the curing reaction (*accelerators*),
- to improve the flow properties (*plasticisers*), and
- to colour the product (*pigments*).

In fact, Novolaks are most commonly used in the manufacture of moulding powders.







**Properties :**

- (a) Phenolic resins are hard, rigid and strong materials ;
- (b) They have excellent heat and moisture resistance ;
- (c) They have good chemical resistance ;
- (d) They have good abrasion resistance ;
- (e) They have good electrical insulation characteristics.
- (f) They are usually dark coloured, Pinkish brown,
- (g) Low molecular weight grades have excellent bonding strength and adhesive properties.

**Applications :** PF resins are generally used for :

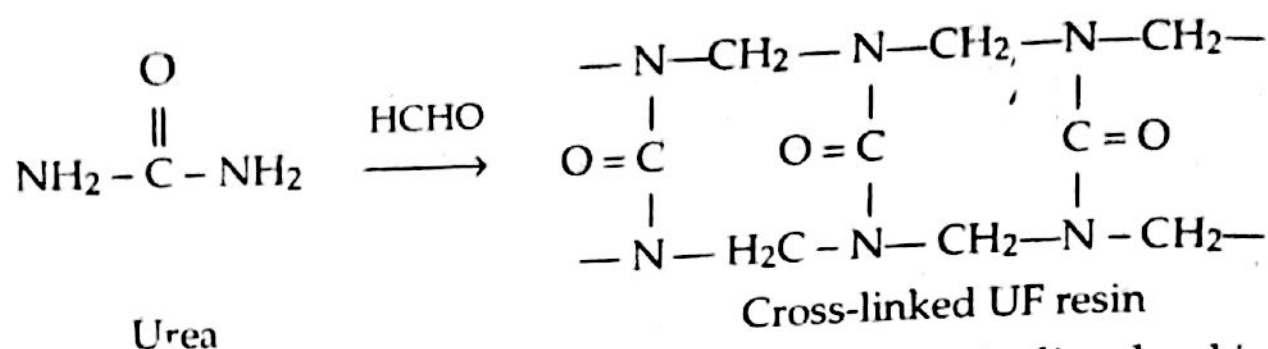
- (a). Domestic plugs and switches,
- (b) Handles for cooker and saucepans,
- (c) Distributor heads of cars,
- (d) Adhesives for grinding wheels and brake linings,
- (e) Impregnating paper, wood and other fillers, for producing decorative laminates and wall coverings and industrial laminates for electrical parts including printed circuits.
- (f) Varnishes, electrical insulation and protective coatings.
- (g) The production of ion-exchange resins.

**9.8 Urea Formaldehyde Resins**

These resins are prepared by the reactions of formaldehyde with urea or melamine to give UF resins and MF resins respectively.

**Urea-formaldehyde Resins****Preparation :**

Urea and formaldehyde react with each other in neutral or acidic conditions to give mono- and Dimethylol urea, which undergo further condensation reactions to give linear, partially cross-linked or fully-cross-linked polymers.



**Manufacture of U-F Moulding Materials.** First urea is dissolved in 36% w/w formalin whose pH is adjusted to 8 with caustic soda. The blending is carried out in stainless-steel reactor for about 30 minutes at 40°C (refer Fig. 19). The urea formaldehyde ratios in the range 1 : 1.3 to 1 : 1.5 are normally employed. A solution at the end of this process contains urea, formaldehyde, mono- and dimethylol urea. Now cellulose fillers are incorporated in it using trough mixer. Generally, dry weight resin-Filler ratio of about 2 : 1 is used. This process of mixing requires 2 hours at 60°C and enables thorough impregnation of the wet base with the resin solution and also advances the resinification reaction. The resulting wet base is then fed to turbine drier. The drying process requires about 2 hours at 100°C and reduces the water content from about 40% to about 6% and also advances the condensation. Now Necessary additives like accelerators, stabilisers, plasticisers, Lubricants and Pigments are incorporated in the dry mixture. The resultant mix is then ball-milled

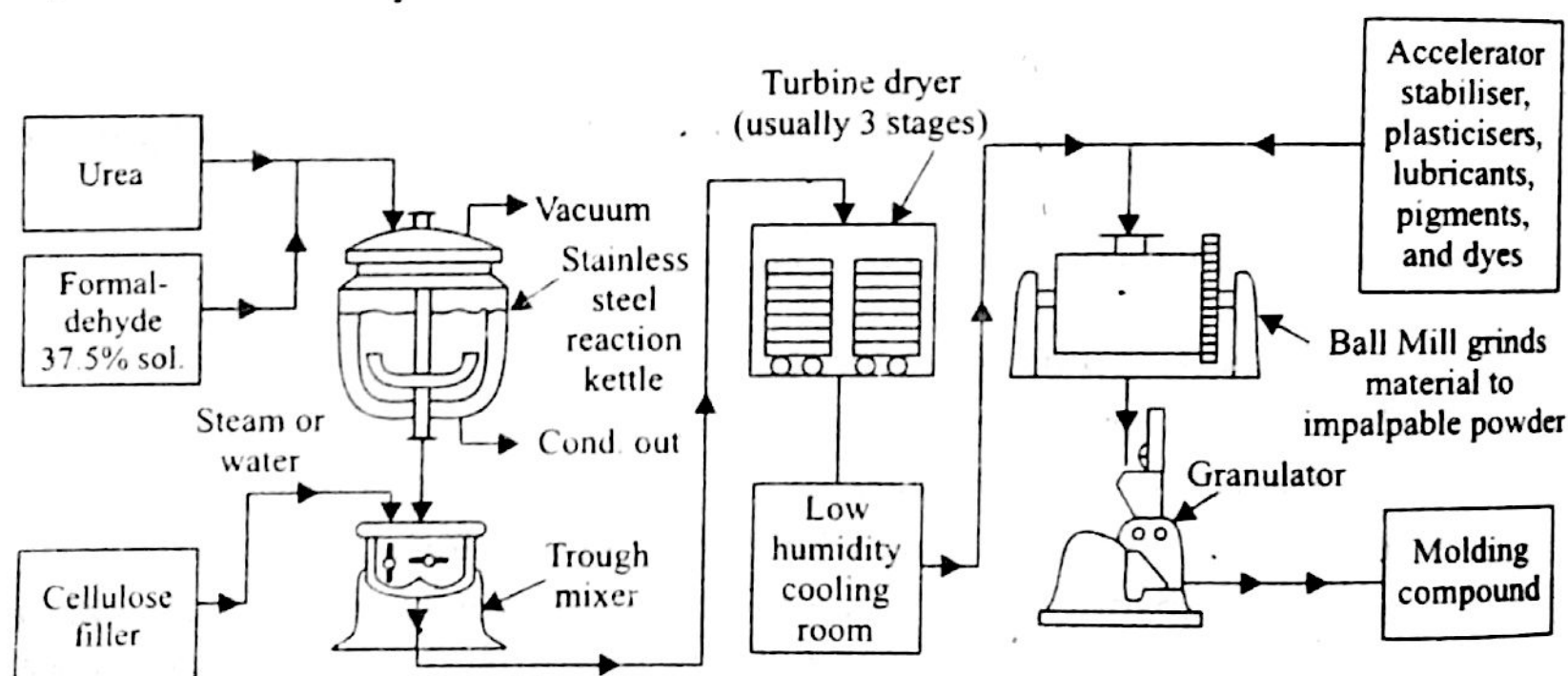


Fig. 19. Flowsheet for Urea Formaldehyde Resin.

for 6-9 hours. Ball-milling process ensures a good dispersion of pigment and gives a fine powder that will produce mouldings of excellent finish. However, the powder has a high bulk factor and problems of air and gas trapping will occur during moulding. Therefore, it is fed to continuous compounder, such as Buss ko-kneder and granulated. Urea-formaldehyde moulding powders, thus obtained, are subsequently moulded on conventional compression and transfer moulding equipment.

**Properties :** The UF resins have the following characteristics :

- They are clear and colourless.
- Better hardness and tensile strength than PF resins,
- Good solvent, grease and moisture resistance.
- Excellent abrasion resistance,
- Good adhesive characteristics.



**Applications :** They are used

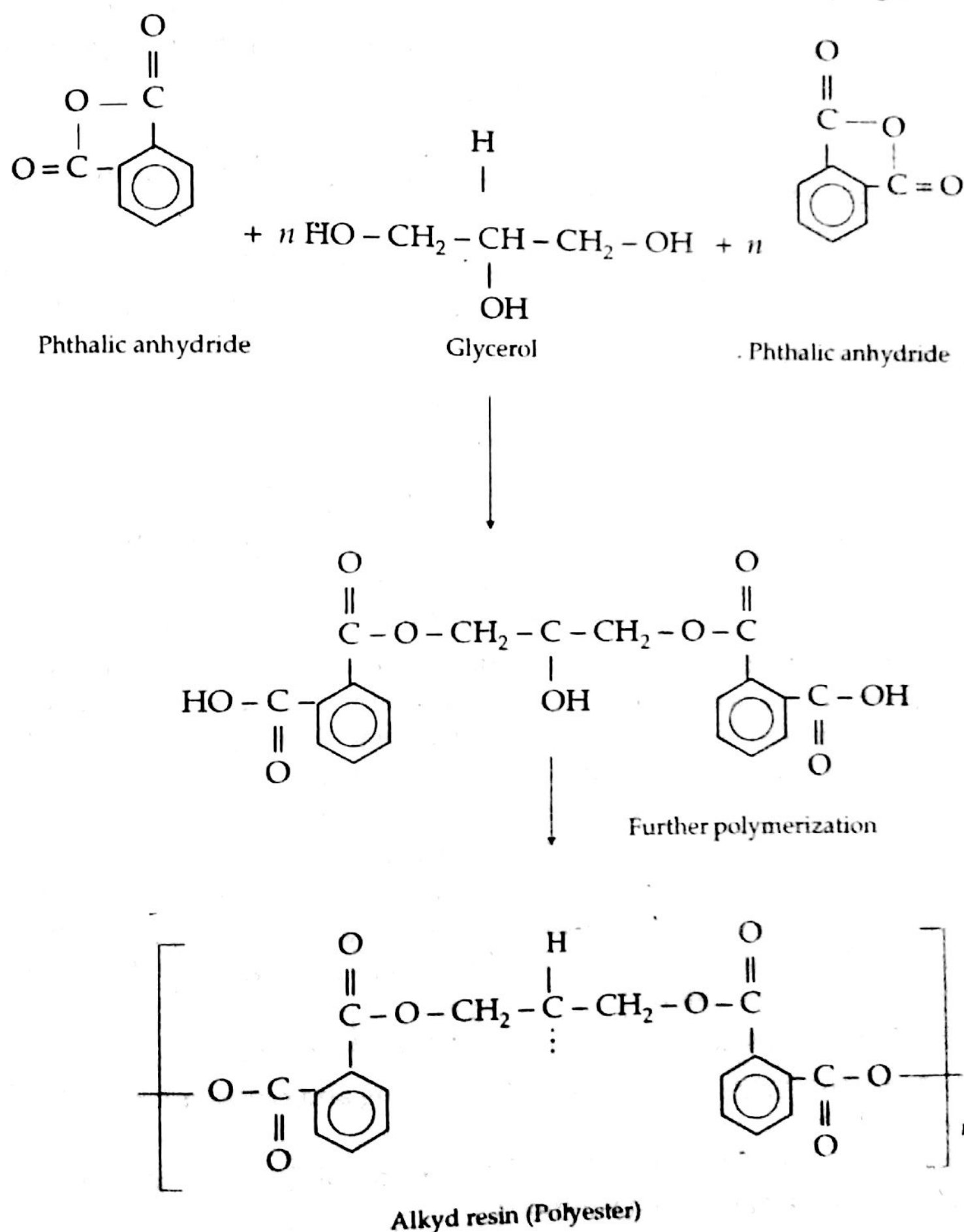
- (a) as Adhesives for plywood and furniture ; (b) for the finishing of cotton textiles. (They impart stiffness, crease resistance, fire-retardation, water repellancy. They are also helpful for shrinkage control). (c) for making buttons, vacuum flask cups and jugs ; (d) for Bottle caps and (e) for coloured toilet seats.

### 9.9 Alkyd Resins (or glyptal resins)

**Preparation.** It is made by the condensation polymerisation of polybasic acids (or anhydride) with polyhydric alcohols (like glycerol) in the presence of heat and catalyst.

As it is obtained from glycerol and phthalic anhydride, the alkyd resin is also known as **glyptal resin**.

They can be modified by adding fatty acid and/or oil (drying or non-drying).



*Properties.* Alkyd resins are :

- (a) hard ;
- (b) resistant towards atmospheric corrosion and acids ;
- (c) insoluble and infusible and
- (d) dimensionally stable.

*Applications.* The alkyd resins are used to make

(a) Paints, enamels and varnishes ; (b) Car Panels and bodies, (c) Binding material for cements, asbestos etc. (d) Circuit-break insulations and (e) Switches and gears.

### 9.10 Silicone Resin

They contain ring structures. They have a much higher cross-link density than is found in silicone elastomer.

In a stretched elastomer, the molecular chains uncoil through rotation about the Si-O-bonds. In a resin, such rotation is highly restricted and the response to stress occurs largely through bending and stretching of bonds.

The properties of resins are a function of R/Si ratio where R is alkyl group.

As the R/Si ratio is lowered from 2 to 1, the polymers become less fluid, less soluble and less fusible.

Most of the resins have R/Si ratio between 1 and 1.6 and their properties are intermediate between those of fluid silicones and those expected of a highly cross linked structure with R/Si ratio equal to 1.

*Preparation :*

- (i) First a mixture of chlorosilanes

$[\text{CH}_3\text{SiCl}_3, (\text{CH}_3)_2\text{SiCl}_2, \phi\text{SiCl}_3, \phi_2\text{SiCl}_2, \phi\text{SiCl}_2]$  is hydrolysed.

During hydrolytic reaction about 90% of silanol groups (*i.e.*, Si-OH groups) condense to form siloxane linkages. In this process of random condensation, some ring closure invariably occurs because of extreme flexibility of Si-O-Si chains.

The remaining 10% of silanol groups condense more slowly and with increasing difficulty because (a) fewer fruitful molecular collisions can now occur since the increasing viscosity renders molecular motion slow. (b) with the growing size of the polymer. The remaining hydroxy groups get fixed in the network too far apart to get condensed with one another. The silanol groups (*i.e.*, Si-OH) left uncondensed in the finished resin impart typical properties to the resin.

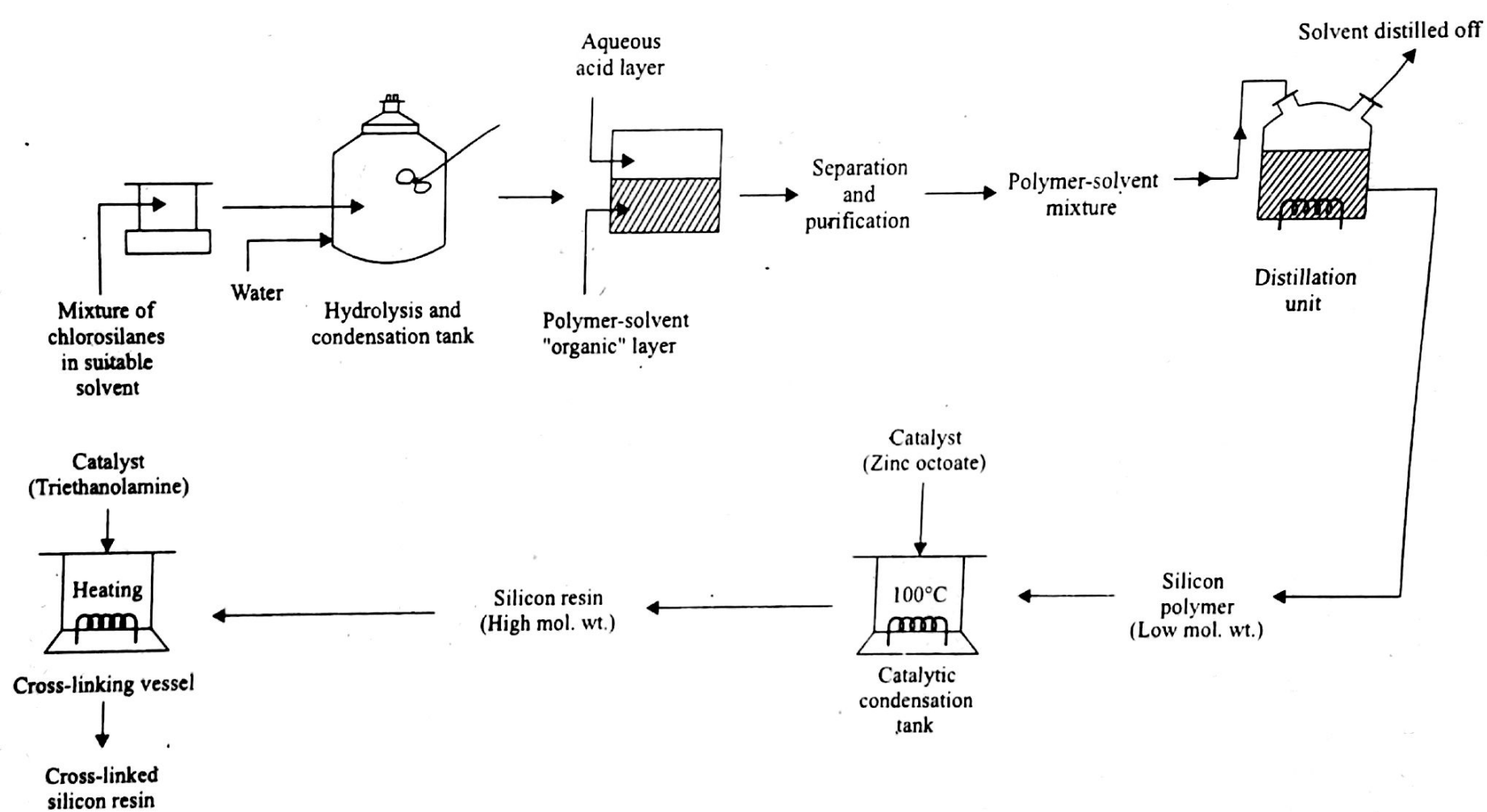
These groups contribute towards viscosity of the product which is an important property that determines the usefulness of a resin. For instance, the viscosity of resin used for laminating purposes should be relatively low so that it may impregnate the glass fibres better.

The silanol groups also determine the shelf life of the resin.

The resins, on storage, constantly go on condensing and cross-linking depending upon temperature.

This type of condensation is extremely slow in solid resins, slow in concentrated solution and fast in dilute solutions.

Fig. 20. Flow sheet diagram for the manufacture of silicon resin.





(ii) After hydrolysis the product is shaken with an organic layer and the organic layer is separated.

(iii) The organic layer is then washed thoroughly to remove the  $\text{Cl}^-$  ions in order to check the reversibility of the hydrolytic reaction.

(iv) Finally curing of the resin is done.

This involves further reaction of the residual silanol groups. The ultimate condensation of these silanol groups occur after the resin is applied. This process can be hastened by heating the resin in the presence of a suitable catalyst. The most common catalysts are metal salts of organic acids such as naphthalates of cobalt, zinc, lead and tin.

**Note.** The nature of the substituents on Si alters the characteristics of the resin.

For example,  $-\text{CH}_3$  group give flexibility,

$-\text{C}_2\text{H}_5$ ,  $-\text{C}_3\text{H}_7$  etc., groups make the resin softer, increase its solubility in organic solvents and increase its water-repellence.

$-\text{C}_6\text{H}_5$  increase resistance towards heat and so on.

### ***Uses of Silicone Resins***

- (i) Used as electrical insulators,
- (ii) Used for coating on metals and for coating cooking pans,
- (iii) Used for lamination purposes.

### **Exercises**

1. What are polymers? Classify them on the basis of structure i.e., Linear, Branched and Crosslinked polymers. Give suitable examples.
2. Differentiate following :
  - (a) Thermoplastic and Thermosetting
  - (b) Homopolymers and Copolymers.
3. Explain Atactic, Isotactic and Syndiotactic polymers.
4. (a) What is meant by degree of polymerisation?  
 (b) What are resins?  
 (c) What is meant by functionality in a monomer?
5. Write short notes on the following :
  - (i) Crystallinity in polymers
  - (ii) Glass transition temperatures ( $T_g$ )
6. Explain the functionality of a monomer.

### **Objective Questions**

#### **A. Multiple Choice Questions**

1. A plastic which can be softened on heating and hardened on cooling is called :  
 (a) Thermite                      (b) Thermosetting    (c) Thermoplastic    (d) Thermoelastic

2. Functionality of phenol is :  
 (a) Four                      (b) Three                      (c) Two                      (d) One
3. Amorphous polymers do not possess any clear  
 (a)  $T_g$                       (b)  $T_m$                       (c) both of these                      (d) none of these
4. Terylene is a  
(a) Polyester                      (b) Polyamide                      (c) Polyglycol                      (d) Polycarbonate
5. Neoprene is a polymer of  
 (a) Isoprene                      (b) Chloroprene                      (c) Butadiene                      (d) Acryl nitrate
6. Terylene is a polymer made by :  
(a) Dimethyl terephthalate and glycol                      (b) Chloroprene  
 (c) Urea and formaldehyde                      (d) Butadiene and styrene
7. Fluorine atoms are present in :  
(a) Teflon                      (b) Styrene                      (c) Nylon                      (d) PVC
8. Which one is a copolymer ?  
 (a) PVC                      (b) Nylon                      (c) Teflon                      (d) Buna-S
9. Bakelite is obtained by the  
(a) Condensation polymerisation                      (b) Copolymerization  
 (c) Addition polymerisation                      (d) None of these
10. Nylon 66 is a  
(a) Polyamide                      (b) Polyester                      (c) Polyacrylate                      (d) Polyglycol

### Answers

- |        |         |        |        |
|--------|---------|--------|--------|
| 1. (c) | 2. (b)  | 3. (b) | 4. (a) |
| 5. (b) | 6. (a)  | 7. (a) | 8. (d) |
| 9. (a) | 10. (a) |        |        |

### B. Fill in the blanks

1. The elasticity of vulcanized rubber \_\_\_\_\_ as the % of sulphur content increases.
2. The trade name of PMMA is \_\_\_\_\_.
3. The repeat unit structure of Buna-S rubber is \_\_\_\_\_.
4. An example of thermosetting addition polymer is \_\_\_\_\_.
5. Phenol-formaldehyde resin is commercially known as \_\_\_\_\_.
6. Natural rubber is a polymer of \_\_\_\_\_.
7. LDPE has a \_\_\_\_\_ melting point than HDPE.
8. An example of plastic used in manufacture of spectacle glass is \_\_\_\_\_.
9. Latex is the dispersion of \_\_\_\_\_ molecules.
10. Nylon 66 and polyester are generally used for preparing \_\_\_\_\_.

### Answers

- |                         |               |  |
|-------------------------|---------------|--|
| 1. Decreases            | 2. Plexiglass | 3. $[\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2]_x [\text{CH}_2 - \text{CH}]_y$ |
| 4. Teflon               | 5. Bakelite   | 6. Isoprene  |
| 8. Plexiglass (or PMMA) |               | 7. Lower   |
|                         |               | 10. Fibers.  |

**RGPV Examination Questions**

1. Mention two important types of synthetic rubbers and discuss their synthesis, properties and applications. [Feb. 2005, 20 marks]
2. (a) What are nylones? How is nylon 66 manufactured? Give flow sheet, state some important uses.  
(b) Discuss the various constituents of plastics and their functions. [Feb. 2005, 20 marks]
3. (a) Discuss the preparation, properties and uses of the following (any three).  
(i) Polystyrene, (ii) Buna-N, (iii) Plexiglass, (iv) Neoprene  
(b) Discuss the manufacture of Nylon 66 with flow sheet. [Dec. 2003, 20 marks]
4. Write short note on vulcanization of rubber. [Dec. 2003, 5 marks]
5. (a) Define and explain giving at least two examples, the following terms :  
(i) Addition polymerization, (ii) Condensation polymerization, (iii) Copolymerization.  
(b) Describe free radical mechanism of polymerisation. [Dec. 2002, 20 marks]
6. Write short notes on any four of the following :  
(i) Bakelite, (ii) Nylon 66, (iii) PVC, (iv) Buna-S, (v) neoprene, (vi) polymethyl methacrylate, (vii) Natural rubber, (viii) Nitrile rubber. [June 2002, 20 marks]
7. (a) How is neoprene prepared? Mention its properties and uses.  
(b) What are silicones? Draw the structure of siloxane polymer obtained by hydrolysing dichlorodimethyl silane. [May 2001, 20 marks]
8. (a) Discuss the manufacture with flow sheet diagram of the following (any two) :  
(i) Polyvinyl chloride (PVC), (ii) Nylon 66, (iii) Dacron (or Terylene).  
(b) Explain why natural rubber needs vulcanization. How is it carried out? [May 2001, 20 marks]
9. (a) Discuss in brief : (i) Neoprene, (ii) Polyurethane, (iii) linear, branched and cross-linked polymers.  
(b) Write short answers of the following :  
(i) What is an elastomer?  
(ii) Natural rubber needs vulcanization, why?  
(iii) GR-S is an example of : (a) Condensation, (b) Copolymerization, (c) Cross-linked polymers, (d) Addition polymerization in which single monomer take part. [Dec. 2001, 20 marks]
10. Write short notes on :  
(i) Thermosetting plastics with examples.  
(ii) Silicon resin. [May 2001, 8 marks]
11. (a) What is gutta percha? How is it different from Hevea and Guayule rubber?  
(b) Name the chemical process which is employed to improve the mechanical strength of natural rubber. How is it formed?  
(c) Describe free radical polymerisation.  
(d) Give flow sheet for producing silicones by Grignard's method.  
(e) Write short note on P.V.C. [June 2004, 23 marks]



## Refractories

*"Character, like porcelain ware, must be printed before it is glazed. There can be no change after it is burned in."*

### 1 INTRODUCTION

The word *ceramics* is derived from Greek word "Keramos" which means burnt stuff. Products made from natural earths that had been exposed to high temperatures were earlier called as ceramics. Now a days ceramics are defined as inorganic, non-metallic materials that are processed and/or used at high temperatures. Most ceramic materials contain silicates, metallic oxides and their combinations.

The important types of ceramic materials, their properties and applications are summarized below in Table 1.

Table 1.

Ceramic Material	Properties	Applications
1. Carborundum, Boron nitride	Hardness and Resistance to wear	Grinding and cutting wheel
2. Cement, brick	Much higher compressive strength than tensile strength	Cement and brick are preferably used in compression than in tension
3. Barium titanate and modified lead zirconate titanate	Piezoelectric property [property of transforming mechanical deformations into voltage changes and vice-versa]	Gramophone pick-ups, Roughness meters
4. Magnesia, Zirconia, Porcelain, alumina etc.	Very good chemical resistance even at very high temperatures	Crucible and furnace linings
5. Glazed porcelain	Excellent chemical resistance	Chemical vessels
6. Glasses	Refractive index easily variable	Manufacture of lens
7. Ferrites	High resistivity and magnetic properties	Electronic applications
8. Refractories	Excellent chemical, heat and Abrasion resistance	Furnace walls and roofs, ladles for pouring metal into mould etc.

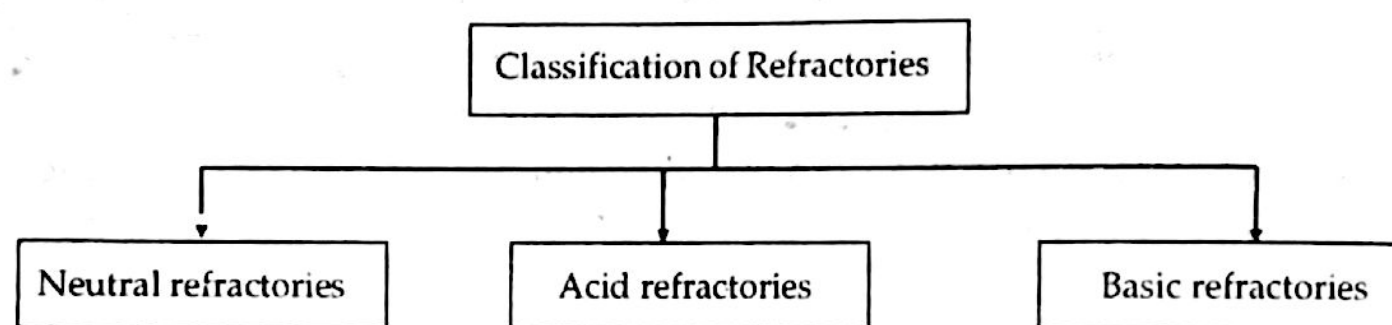
The existence of many ceramic materials with quite different properties is due to the fact that many combinations of the metallic and non-metallic atoms, with several structural arrangements for each combination, are possible. The constituents of ceramic material may form covalent or ionic bonds. Most of the ceramics are insulators like other covalent materials. They are highly stable and have high melting points which indicate that there exists ionic bonding as well in them.

## 2 REFRACTORIES

*Refractories* are ceramic materials that can withstand high temperatures as well as abrasive and corrosive action of molten metals, slags and gases, without suffering a deformation in shape. The main objective of a refractory is to confine heat.

### Classification of Refractories

On the basis of the chemical properties of their constituent substances, refractories are classified into three categories :



(a) *Neutral refractories* like graphite, zirconia and SiC (carborundum) refractories. These refractories are made from weakly basic/acidic materials like carbon, zirconia ( $\text{ZrO}_2$ ) and chromite ( $\text{FeO} \cdot \text{CrO}_2$ )

(b) *Acid refractories* like alumina, silica and fire clay refractories. These refractories consist of acidic materials like alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ). These refractory materials are resistant to acid slags (like silica) and are often used as containment vessel for them. On the other hand, they are readily attacked by basic slags (like  $\text{CaO}$ ,  $\text{MgO}$  etc.) and contact with these oxide materials should be avoided.

(c) *Basic refractories* like magnesite and dolomite refractories. These refractories consist of basic materials like  $\text{CaO}$ ,  $\text{MgO}$  etc. and are especially resistant to basic slags. That's why they find extensive use in some steel making open hearth furnaces. The presence of acidic materials like silica is deleterious to their high-temperature performance.

### Characteristics of refractory materials

- (i) A good refractory material should have excellent heat, corrosion and abrasion resistance ;
- (ii) It should possess low thermal coefficient of expansion and should expand and contract uniformly, with increase and decrease of temperature respectively ;
- (iii) It should possess high fusion temperature. It should be infusible at the temperature to which it is liable to be exposed ;
- (iv) It should be able to withstand the overlying load of structure, at operating temperatures.

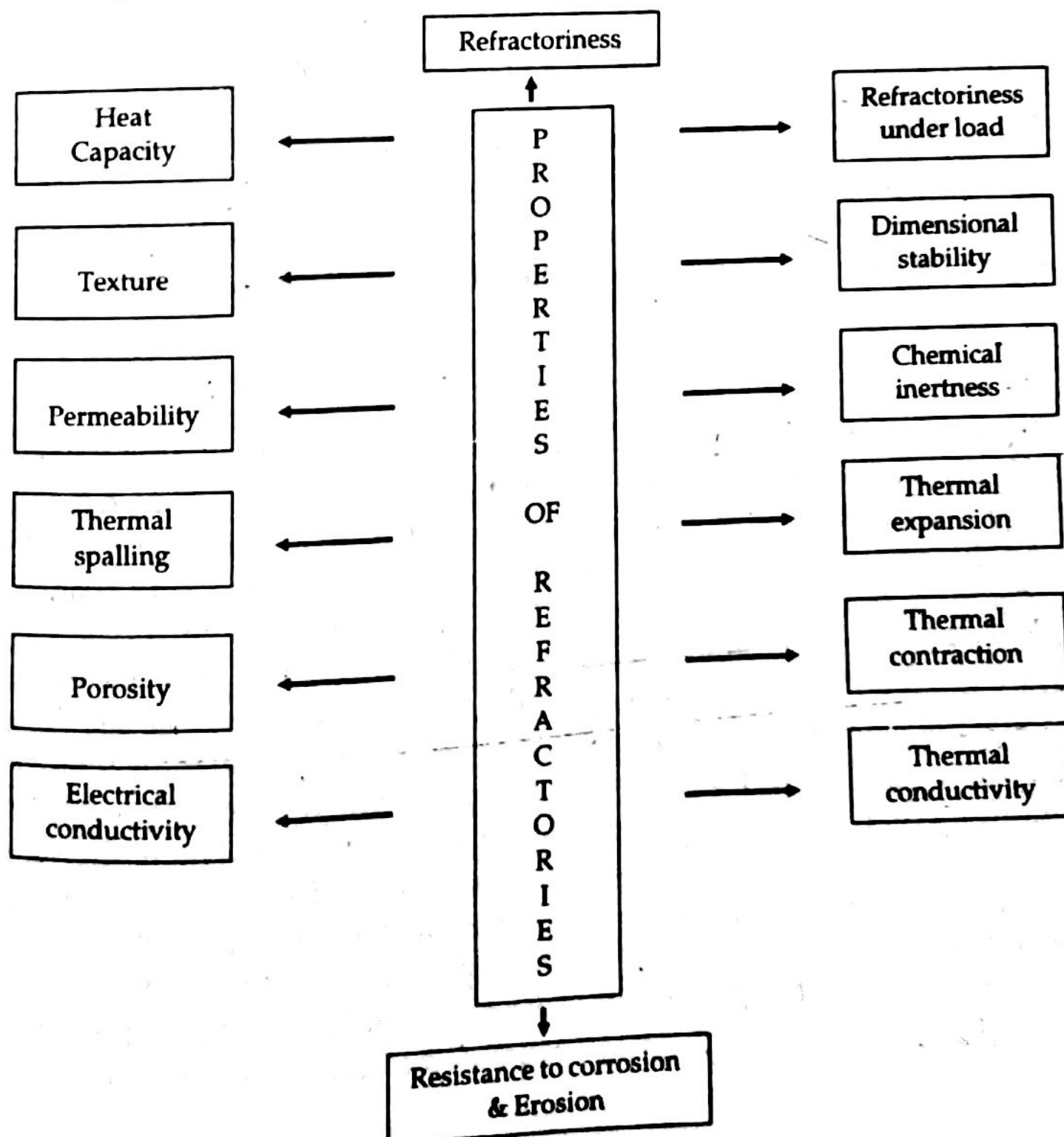
- (v) They should be chemically inert towards corrosive action of molten metal, gases and slags, produced in its immediate contact in furnaces.
- (vi) They should not crack at the operating temperatures.

If a given refractory material does not have the above mentioned characteristics, it will fail in service. Thus, we can easily summarize *conditions which lead to failure of a refractory material* as :

- (i) Using a refractory material which do not have required heat, corrosion and abrasion resistance ;
- (ii) Using refractory material of higher thermal expansion ;
- (iii) Using a refractory of refractoriness less than that of the operating temperature ;
- (iv) Using lower-duty refractory bricks in a furnace than the actual load of raw materials in products ;
- (v) Using basic refractory in a furnace in which acidic reactants and/or products are being processed and vice-versa ;
- (vi) Using refractories which undergo considerable volume changes during their use at high temperature.

### 3 PROPERTIES OF REFRACTORIES

The important properties are summarized in figure and discussed thereafter :





(a) **Refractoriness.** "It is the ability of a refractory material to withstand the heat without appreciable softening or deformation under given service conditions." It is generally measured as the softening temperature. It is necessary that a refractory material should have a softening temperature higher than the operating temperature of the furnace in which it is to be used. Sometimes, it can be employed to withstand a temperature higher than its softening temperature since the outer part of refractory is at a lower temperature and still in solid state, providing strength. Thus, refractory material does not melt away although inner refractory lining in a furnace is at a much higher temperature than the outer ones. Most of the commercial refractories do not exhibit sharp melting points and they soften gradually over a range of temperatures. This is due to the fact that they are composed of several minerals, both crystalline and amorphous in nature. Fusion temperatures of some neutral, acidic and basic refractories are given in Table 2.

**Table 2 : Fusion Temperatures of Neutral, Acidic and Basic refractories**

S.No.	Refractory type	Refractory material	Fusion temperature (°C)
1.	Neutral	Graphite (C)	3500
2.	Neutral	Zirconia ( $ZrO_2$ )	2710
3.	Neutral	Silicon carbide (SiC)	2700
4.	Acidic	Alumina ( $Al_2O_3$ )	2050
5.	Acidic	Silica brick ( $SiO_2$ )	1700
6.	Acidic	Fire clay brick	1600-1750
7.	Basic	Magnesia brick	2200

**Measurement of Refractoriness.** The softening temperatures of refractories are generally determined by *seger cones* (also called *pyrometric cones*) test. In this test, behaviour of heat on cone of refractory (to be tested) and series of seger cones of standard dimensions are compared. These cones are small pyramid shaped with triangular base, 38 mm high with 19 mm long sides. The test refractory in the form of a cone is kept along side similar sized standard cones and all are heated uniformly at 20°C/hr or 100°C/hr or 150°C/hr or occasionally at 600°C/hr. As seger cones are made of a particular refractory of a definite softening temperature so they are assigned ascending seger cone numbers with increasing softening temperature. When the test cone softens and loses its shape, one of the standard seger cone also softens and loses its shape provided its refractoriness is close to that of the test cone. The serial number of this standard seger cone is noted and this number is the *Pyrometric cone equivalent (PCE)* of the refractory under that test. When the test cone softens earlier than one standard cone, but later than the previous one, the PCE value of the test sample is approximated as average of the two.

The temperature at which the softening or fusion of the test-cone occurs is indicated by its apex touching the base, see Fig. 1.

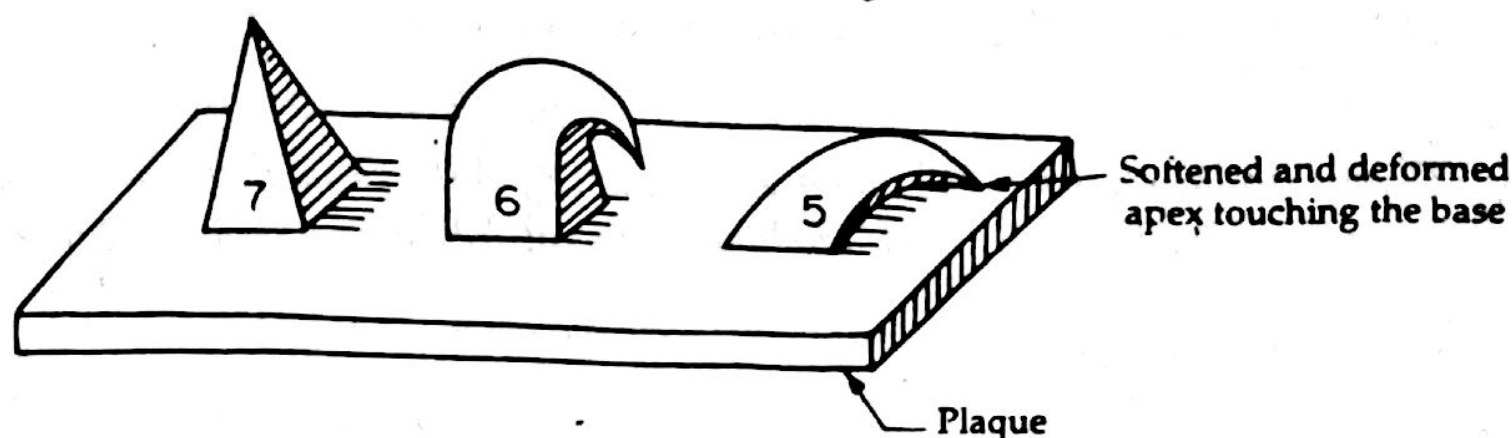


Fig. 1. Seger cone-test.

Table 3 : Seger-cone numbers and fusion temperatures of seger cones at 10°C/minute heating rate

Seger-cone number	Temperature ( °C)
1	1110
5	1180
10	1300
15	1435
20	1530
30	1670
35	1770

(b) **Refractoriness-under-Load (or Strength).** Temperature resistance and load bearing capacity are the two essential qualities of a refractory. This is due to the fact that commercial refractories which are used for lining high temperature furnace are expected to withstand varying loads of the charge. Hence they should possess high strength and excellent temperature resistance.

**Measurement.** Seger cone test is not applicable for the measurement of strength. Because, some refractories soften gradually over a range of temperature, but under appreciable load, they collapse, far below their true fusion temperature. High alumina bricks and fire-clays are examples of such refractory materials. There are some other refractory materials like silica bricks which exert good load bearing characteristics upto their fusion temperatures as they soften over a relatively narrow range of temperature. Thus, for good results, Refractoriness-Under-Load (R.U.L.) test is performed by applying a load of (3.5 or 1.75 kg/cm<sup>2</sup>) to the refractory specimen (of size 5 cm<sup>2</sup> and 75 cm high). The sample is then kept in carbon-resistance furnace and heating is started at the rate of 10°C/minute. The height of the specimen is plotted vs. temperature and R.U.L. is expressed as the temperature at which 10% deformation takes place.

Based on R.U.L. test, refractory materials are classified into following three categories :

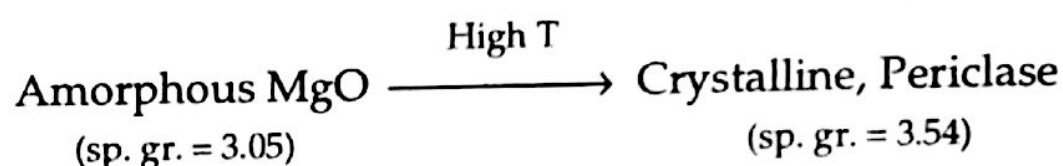
- (i) **A high heat-duty brick,** (which does not deform more than 10 percent at 1350°C).

- (ii) *An intermediate heat-duty brick, (which does not deform more than 10% at 1300°C).*
- (iii) *A moderate heat-duty brick (which does not deform more than 10% at 1100°C).*

(c) **Dimensional stability.** "Dimensional stability is the resistance of a material to any change in volume when it is exposed to high temperatures, over a prolonged time."

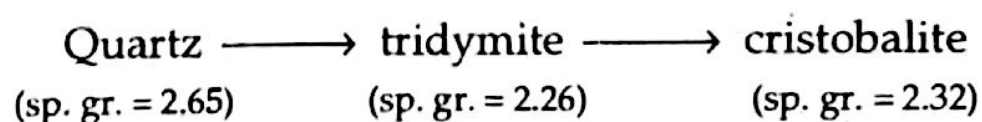
#### *Types of dimensional changes*

(i) **Permanent contraction.** When a refractory is subjected to high temperatures for long duration, either low fusible constituent melts away forming liquid which fills the pores of the refractory body causing shrinkage and vitrification. (Fireclay brick show such type of behaviour) or transformation of one crystalline form of material into another more dense form can also take place. For example, consider magnesite brick :



With the increase in density, there is shrinkage in magnesite brick.

(ii) **Permanent expansion.** Transformation of one crystalline form of refractory into another of low density leads to expansion when a refractory is subjected to high temperatures for longer duration. Silica brick is one such example, which undergoes permanent expansion in service. For instance, crystalline transformation in silica brick is given below :



(d) **Chemical inertness.** The refractory material which is used as liner for furnace walls should be chemically inert to the chemicals charged into a furnace. It should not react with the reactants, slags, furnace gases, fuel ashes and the products involved inside the furnace. Such reactions can contaminate the product and/or gradually corrode the furnace. Hence, it is inadvisable to employ an acid refractory in contact with an alkaline product or vice-versa.

(e) **Thermal expansion and contraction.** A good refractory material should have least possible coefficient of thermal expansion. Since like other materials, refractory also expands when heated and contract when cooled. Repeated expansion and contraction contribute much towards rapid wear and tear of the refractory structure and its rapid breakdown. Sustained strong binding between the refractory lining and base structure and within the refractory matter is possible only when the thermal effect or volume (coefficient of expansion) is negligible. Due to thermal shock, a substandard refractory develops cracks and then detaches itself from the furnace wall. It is essential therefore, allowance has to be made for thermal expansion.



(f) **Thermal conductivity.** It is amongst one of the important properties of refractory material since it determines the amount of heat transmission or heat loss due to radiation through it.

Refractories with low thermal conductivities are used for lining the walls of blast furnace, copper hearth furnace etc. because they minimize the heat losses to outside by radiation and help in the maintenance of high temperatures inside the furnace. On the other hand, refractories with high thermal conductivities are used for lining the walls of muffle furnace, coke-oven retorts etc. because in these cases efficient heat transfer from the outer surface to charge is needed.

Hence, depending upon the type of furnace, refractory materials of high or low thermal conductivities are required by industrial operations.

(g) **Resistance to Corrosion and Erosion.** The higher temperatures at which the furnace is operated, viscosity of slag decreases which accelerate the chemical reaction between the slag and refractory lining. This might lead to corrosion of refractory lining. Greater wetting of the refractory by the slag also increases corrosion. *Erosion* is gradual wearing away of a material from its surface due to the mechanical action of flue gases escaping at high velocities, carbon-particles and descending hard charge inside the furnace. Erosion produces cavities on the surface of refractories which in turn increase the probability of corrosion.

For a refractory to last longer, it is desirable that it should have excellent corrosion and erosion resistance. This property is very important for the selection of refractory material for by-product coke-oven wall and lining of discharge ends of rotary cement kilns etc.

(h) **Electrical conductivity.** A refractory material of low electrical conductivity is desired for lining the walls of electrical furnace. For proper selection of refractory material it should be always remembered that electrical conductivities of these material increases with rise in temperature. In general, all refractory materials, (except graphite) are poor conductors of electricity.

(i) **Porosity.** Porosity of a refractory material is the ratio of its pore's volume to the bulk volume. Pores are present in all refractory materials and these can be open or closed. Porosity affects many characteristics of a refractory material. For instance, flue gases, slag and/or molten charge can penetrate to greater depth and may react and reduce the life of refractory material of porous refractory. Porosity can also increase the thermal shock resistance. In addition, air is entrapped in the pores and increase the insulation characteristics of porous bricks. In contrast, the densest and least porous bricks have the highest thermal conductivity, strength, resistance to abrasion and corrosion.

(j) **Thermal spalling.** Rapid changes in temperature, cause uneven expansion and contraction of refractory material, thereby leading to development of internal stresses and strains. This in turn are responsible for cracking, breaking or fracturing of a refractory brick or block under high temperature, collectively known as *thermal spalling*. Thermal spalling can also be caused by the variation in the coefficient of expansion due to slag penetration in the refractory brick. A good refractory must show a good resistance to thermal spalling. Thermal spalling can be decreased by minimising the development of internal stresses by :

- (i) Using a refractory with high porosity, good thermal conductivity and low coefficient of expansion,
- (ii) Avoiding sudden temperature changes,
- (iii) Proper furnace design.

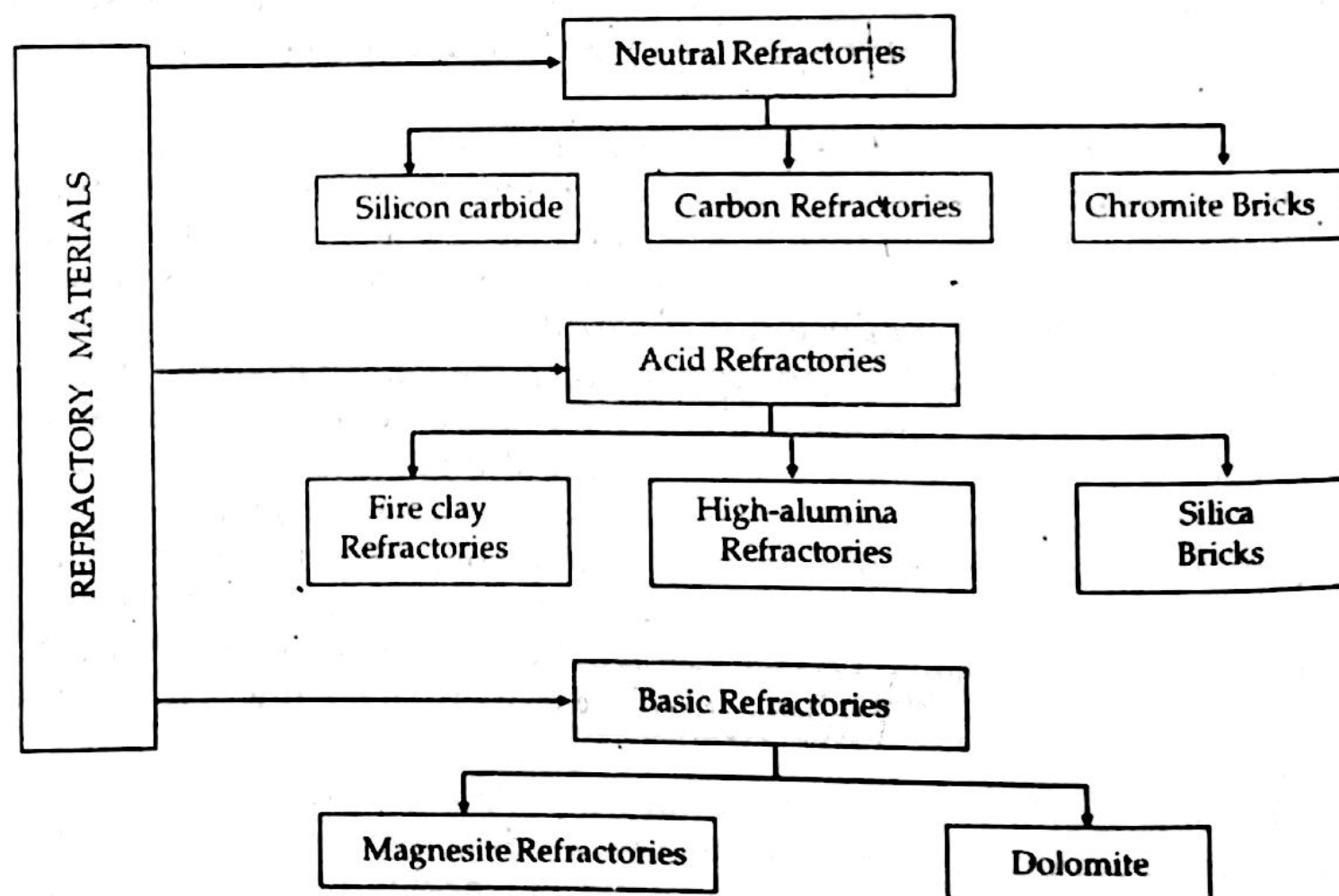
(k) **Permeability.** "It is a measure of rate of diffusion of molten solids, liquids and gases through the connected pores of refractory." The higher the porosity of a refractory brick, the more easily it is penetrated by gases and molten fluxes. Permeability depends on the size and number of connected pores. A good refractory material should show low permeability.

(l) **Texture.** Texture can be coarse or fine. Porosity of coarse or light textured bricks are higher than fine or dense-textured bricks. That's why coarse textured refractory bricks have

- (i) good resistance to thermal spalling,
- (ii) low crushing strength, and
- (iii) low abrasion and corrosion resistance.

(m) **Heat capacity.** The dense and heavy fire-clay bricks have higher heat capacity and as such are best suited for regenerators, checker-works as in stoves for blast furnaces, coke ovens, glass furnaces etc. In contrast, intermittently operated furnaces require refractory material of low heat capacity (i.e., light weight refractory brick). Because in them working temperature of the furnace is achieved with lesser consumption of fuel and in lesser time.

#### 4 SOME IMPORTANT HIGH REFRACTORY MATERIALS



Three important classes of Refractory materials

##### 1. Neutral Refractories

###### (i) Silicon carbide (carborundum) Refractories

**Preparation :** Carborundum is made by heating a mixture of coke (40%) and sand (60%) together with some saw dust (it helps in increasing the porosity) and salt (it helps in the removal of iron etc., in the form of volatile chlorides) in an electric furnace at 1500 °C. The SiC in the form of interlocked crystals are formed.



by this method. These interlocked crystals are crushed ; sized and suitably graded for getting dense packing. These are then mixed with bonding agents ( $\leq 10\%$ ) like plastic, fire clay, graphite or silicon nitride for imparting superior oxidation resistance. After mixing with bonding agent, final firing is done in reducing atmosphere at about  $1500^{\circ}\text{C}$ . It is interesting to note here that if SiC particles are mixed with glue (temporary binding agent) and fired at  $2000^{\circ}\text{C}$ , self-bonding type of SiC refractory bricks (having intercrystalline bonds) results.

**Properties :** (a) SiC refractories have high thermal conductivity, low thermal coefficient of expansion and thus have ability to withstand sudden temperature fluctuations.

(b) The SiC bricks are extremely refractory and possess high mechanical strength. They can withstand loads in furnaces even at higher temperatures ( $\geq 1650^{\circ}\text{C}$ ). They possess excellent resistance to spalling and abrasion.

(c) Chemical resistance of SiC refractories are also good. They have high resistance to reducing atmosphere and acid slag, medium resistance to oxidising atmosphere and low resistance to basic slag.

In oxidising atmosphere, at temperature of about  $950^{\circ}\text{C}$ , SiC bricks have a tendency to oxidize to Si. This tendency can be minimized by thin layer of zirconium coating.

**Applications :**

- (a) SiC refractories (lime bonded), are mainly used in muffles, because of their good thermal conductivity,
- (b) It is also an ideal choice for recuperaters because of good resistance to spalling under repeated temperature fluctuations and ability to absorb and release heat rapidly,
- (c) Partition walls of chamber kilns, coke ovens and furnace floors are also made by SiC bricks,
- (d) Globars (furnace's heating elements in the form of rods and bars) are also made by SiC refractory because of its high electrical conductivity.
- (e) High conductivity crucibles are made from SiC bonded with tar.

**(ii) Carbon Refractories**

**Preparation :** They are made by mixing either crushed coke with pitch (or tar) or graphite with clay and firing at about  $1300 - 1400^{\circ}\text{C}$ . The space between the bricks is filled with a mixture of sand and powdered coke for minimizing contact of the bricks with air during firing.

**Properties :**

- (a) Carbon and graphite refractories are practically infusible and can withstand temperature fluctuations,
- (b) They have high thermal conductivity,
- (c) They are excellent refractory materials in neutral or acidic conditions because in oxidizing atmosphere (say in air). They get readily oxidized particularly at elevated temperatures.



**Applications :**

- (a) Carbon and graphite bricks are mostly used as construction materials for electrodes.
- (b) They are also used for linings of chemical resistant equipments, atomic reactors, electric furnaces, heat-transfer systems; and in aluminium, copper and lead smelting furnaces.
- (c) Crucibles made from graphite are also widely used in industry. The crucible surface is coated with boric acid, borax, soda ash, sodium silicate,  $\text{CaCl}_2$  or  $\text{MgCl}_2$  in order to prevent oxidation.

**Note :** Clay or carbon bonded graphite crucibles upto 100 kg capacity are produced by small scale sector in India.

**(iii) Chromite Bricks**

**Preparation :** Chromite ( $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ ) is blended with clay and then firing is done at a temperature of 1500 to 1700°C for the manufacture of chromite bricks.

**Properties :**

- (a) Chromite bricks are neutral refractories having good slag resistance.
- (b) Their spalling resistance is moderate.
- (c) They possess moderate thermal conductivity & high density.
- (d) Their use temperature is limited to 1800°C.
- (e) They have good crushing strength and refractoriness under load.

**Applications :** Chromite bricks are used in :

- (a) Furnace linings,
- (b) Sodium carbonate recovery furnaces &
- (c) bottoms of soaking pits.

**II. Acid Refractories****(i) Fire clay refractories**

**Preparation :** Fire clay refractories are made from raw and calcined aluminosilicate which are known as fire clays because they can withstand high temperatures. Calcined fire clay, known as the "Grog", accounts for 50% or more of the batch mix. The exact properties of the constituents depend on the type of bricks to be made. For example, feebly acidic fireclay bricks contain 55%  $\text{SiO}_2$  and 35%  $\text{Al}_2\text{O}_3$  while nearly neutral fire clay bricks contain 40%  $\text{SiO}_2$  and 55%  $\text{Al}_2\text{O}_3$ . The balance in both of them consists of  $\text{K}_2\text{O}$ ,  $\text{FeO}$ ,  $\text{CaO}$ ,  $\text{MgO}$  etc. (Accessory oxides in the clay).

**Properties :**

- (a) Depending on the content of iron oxides, fireclay bricks are light yellow to reddish-brown in colour.
- (b) Depending on the  $\text{SiO}_2$  content, the fireclay bricks show acidic character.
- (c) Depending on the percentage of grog, these materials show resistance to thermal spalling. Greater is the % of grog, greater will be the resistance to thermal spalling.
- (d) They also have high crushing strength (about 200  $\text{kg/cm}^2$ ) which goes down with increasing temperatures.
- (e) Properly fired bricks are as hard as steel.

**Applications :**

- (a) Fire clay refractories are mostly consumed by steel industries as these are used for the lining of blast furnaces, open hearths, stoves, ovens, crucible furnaces etc.
- (b) These are also widely used in foundries ; lime, continuous ceramic, pottery and metallurgical kilns ; glass, brass and copper furnaces ; cupolas etc.

**(ii) High-alumina Refractories**

When the alumina ( $\text{Al}_2\text{O}_3$ ) content in the fire clay brick reaches above 47.5% then it is called high-alumina brick.

**Preparation :** It is made by mixing calcined bauxite ( $\text{Al}_2\text{O}_3$ ) with clay bind.

**Properties.** Because of the high alumina content, these bricks have more refractoriness, better slag resistance, inertness to CO and stability to natural gas environment upto  $1000^\circ\text{C}$ .

**Applications :** High alumina refractories having 75%  $\text{Al}_2\text{O}_3$  are known as 'high-duty bricks' and find applications in the hottest zones of cement rotary kilns, combustion zones of oil-fired furnaces, aluminium melting furnaces etc.

High alumina refractories containing 50 to 60%  $\text{Al}_2\text{O}_3$  are known as 'medium-duty bricks' and find applications in linings of portland cement rotary kilns, soaking pits, reheating furnaces, hearths and walls, etc., which are subjected to high abrasion.

**(iii) Silica Bricks**

**Preparation.** The raw materials used for the manufacture of silica bricks are quartz, quartzite, sand, sandstone, ganister etc. Siliceous rock is first crushed and ground with 2% lime & water. The resultant thick paste is then made into bricks by machine pressing. After drying, bricks are burnt in kilns. In about 24 hours, the temperature is slowly raised to about  $1500^\circ\text{C}$ . This high temperature is maintained for about 12 hours. This step is essential since it allows quartzite to be converted into cristobalite (allotropic transformation) careful cooling is then done & it takes about 1 to 2 weeks. Cristobalite is slowly changed into tridymite during cooling and in the final brick, the mixture of two results.

**Properties :**

- (a) Silica bricks are yellowish in colour with brown specks throughout the body
- (b) These bricks are acidic & are therefore suitable for acidic furnace charges.
- (c) Silica bricks are remarkable for their load bearing capacity. They can withstand a load of about  $3.5 \text{ kg/cm}^2$  upto about  $1600^\circ\text{C}$ .
- (d) Silica bricks are not susceptible to thermal spalling at temperature below  $800^\circ\text{C}$
- (e) These bricks are light & possess high rigidity & mechanical strength.
- (f) These bricks do not contract in use.

**Applications :**

Silica bricks are used in lining roof arches of open hearth furnaces & reverberatory furnaces, gas retort and walls of coke ovens.



### III. Basic Refractories

#### (i) Magnesite Refractories

**Preparation :** It is made from dead-burnt magnesite grain which are properly crushed into powder form of proper size. Molasses or sulphite lye is used as a binder. Thermal shock resistance is imparted to the magnesite refractory by adding 2 to 6% of alumina. The ingredients are blended after adding requisite quantity of water and the mix is aged for 1 to 10 days to ensure complete hydration of any free lime present. The mix is then moulded into bricks and temperature is slowly increased to  $1500^{\circ}\text{C}$ . The bricks are kept at this temperature for about 8 hrs. and then slowly cooled.

**Properties :**

- (a) Magnesite refractories have high resistance to basic slag and low resistance to acid slag.
- (b) They possess good crushing strength.
- (c) It can be used up to  $2000^{\circ}\text{C}$  without load and under a load of  $3.5 \text{ kg/cm}^2$ , it can be used up to  $1500^{\circ}\text{C}$ .
- (d) It has poor resistance to abrasion and spalling.

**Applications :**

- (a) Mainly used in steel industry for the lining of basic converters and open-hearth furnaces.
- (b) These refractories are also used in the roofs of non-ferrous reverberating furnaces e.g., those used for Pb, Cu and Sn.
- (c) Also used for the lining of refining furnaces for gold, silver and platinum etc.

#### (ii) Dolomite Refractories

**Preparation :** After washing and crushing, Dolomite (mixed carbonate of calcium and magnesium,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ ) is calcined. Dolomite decomposes to give  $\text{CaO}$  and  $\text{MgO}$  during calcination. This is then mixed with silicate (which acts as binder) and water. The mixture is allowed to stand for sometime and then moulded into bricks. The bricks are then fired at  $1500^{\circ}\text{C}$  for about 24 hrs. in a kiln.

**Properties.** Compared to magnesite bricks, dolomite bricks possess

- (a) less strength and low resistance to thermal shock,
  - (b) more softness and porosity and hygroscopicity and greater shrinkage.
- Stabilized dolomite bricks do not have the above mentioned limitations and it is made by incorporating serpentine ( $\text{MgO} \cdot \text{SiO}_2$ ) in dolomite before calcination in the initial stages. Stabilized dolomite bricks have very good resistance to basic slags.

**Applications :**

- (a) Dolomite refractory is generally used as a repair material.
- (b) Stabilized dolomite refractory is used for basic electric furnace linings, ladle linings, open-hearth furnaces etc.
- (c) Stabilized dolomite refractory material is also used as cheap substitute for magnesite bricks.



### Exercises

1. How are refractories classified ? State some important applications of refractories.
2. Write short notes on :  
(a) Silica refractories, (b) Magnesite refractories.
3. What are the causes for failure of a refractory ?
4. Give an account of the preparation, properties and uses of the following :  
(i) Dolomite refractories, (ii) Fire clay refractories,  
(iii) High alumina refractories, (iv) Silica refractories.
5. What is the importance of the following properties in the evaluation of a refractory brick :  
(i) Thermal spalling ; (ii) Refractoriness under load ;  
(iii) Dimensional stability ; (iv) Thermal conductivity ;  
(v) Porosity ; (vi) Heat capacity.
6. What are acidic refractories and how these differ from basic refractories ?

### R.G..PV. Examination Questions

1. Explain briefly the industrial uses of refractories. [Feb. 2005, 5 marks]
2. Write short notes on the following :  
(a) Silica refractory.  
(b) Thermal spalling.  
(c) Pyrometric cone equivalent. [Dec. 2003, 15 marks]
3. (a) Fill up the blanks in the following :  
(i) Refractoriness of a material is defined as .....  
(ii) Porosity of a refractory material is given by the ratio of .....  
(iii) Thermal spalling means .....  
(iv) The heat capacity of furnace depends upon the following three factors namely .....  
(v) Dimensional stability of a refractory indicates .....  
(b) Give an account of the preparation, properties and uses of silica bricks. [Dec. 2000, 5 + 7 marks]
4. (a) Define and classify refractories with example.  
(b) Which of the following is neutral refractories :  
(A) Dolomite bricks (B) Fireclay bricks  
(C) Silica bricks (D) Chromite bricks  
(c) Describe any two important properties of refractories. [June 2002, 5 marks]
5. What are the causes of failure of refractory ? [Dec. 2001, 5 marks]
6. Define and classify refractories with example. [June 2001, 7 marks]
7. Write short note on refractories and thermal spalling. [June 2003, 7 marks]
8. Write short note on natural refractories. [June 2004, 3 marks]

# Instrumental Techniques in Chemical Analysis

"We can never know for certain the truth of the substance underlying what we get through the senses. Why should the doubt be greater in the case of the entity behind the ideas which are the creation of mind?"

## 1 INTRODUCTION

Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanical selection rules.

Let us first discuss the *origin of Spectrum*. Consider two energy levels of an atom/molecule. The one with lower energy is called ground state energy level ( $E_g$ ) and the one with higher energy is called excited state energy level ( $E_e$ ).

**Absorption spectrum** results when an atom or molecule undergoes a transition from the lower energy level to the higher one with the absorption of a photon of energy  $h\nu$ . Provided  $h\nu$  is exactly equal to the energy difference,  $\Delta E = E_e - E_g$  between the two levels. See Fig. 1.

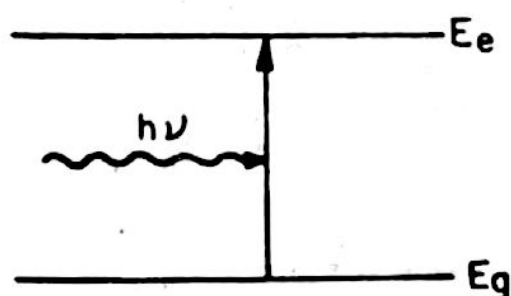


Fig. 1. Absorption Spectrum

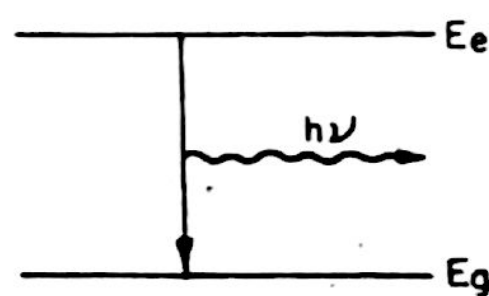


Fig. 2. Emission Spectrum

**Emission spectrum** results when the atom or molecule falls from the excited state to the ground state with the emission of a photon of energy  $h\nu$ , see Fig. 2.

Thus, spectra can be broadly classified into two categories.

(1) **Atomic spectra.** Which arises from the transitions of an electrons between the atomic energy levels.

(2) **Molecular spectra.** Which arises from the transitions of an electron between the molecular energy levels.

**Importance of Spectroscopy.** Molecules are of so infinitesimal dimensions that it is not possible to see them. Our knowledge of molecular structure is indirectly derived from spectroscopy.

### Molecular Spectroscopy

Let us first discuss the different types of energies associated with a given molecule.

The molecule possesses *electronic energy* which is associated with the transition of an electron from the ground state energy level to the excited state by the absorption of photons of suitable frequency.

When the centre of gravity does not change during the to-and-fro motion of the nuclei of the molecule, the molecule is said to possess *vibrational energy*.

Consider an axis perpendicular to the internuclear axis and passing through the centre of gravity of the molecule if the molecule rotates about this axis, it requires *rotational energy*.

During the motion, if the centre of gravity of molecule changes the molecule possesses *translational energy*.

The total energy of the molecule ( $E$ ) is sum of electronic energy ( $E_{el}$ ), vibrational energy ( $E_{vib.}$ ), rotational energy ( $E_{rot.}$ ) and translational energy ( $E_{tr.}$ )

The total energy of a molecule, according to *Born-Oppenheimer approximation* is given by sum of all these energies viz.

$$E = E_{el} + E_{vib.} + E_{rot.} + E_{tr.} \quad \dots(1)$$

Moreover,  $E_{el} \gg E_{vib} \gg E_{rot} \gg E_{tr}$

and as the translational energy is negligibly small, we write the Born-Oppenheimer approximation as

$$E = E_{el} + E_{vib} + E_{rot.} \quad \dots(2)$$

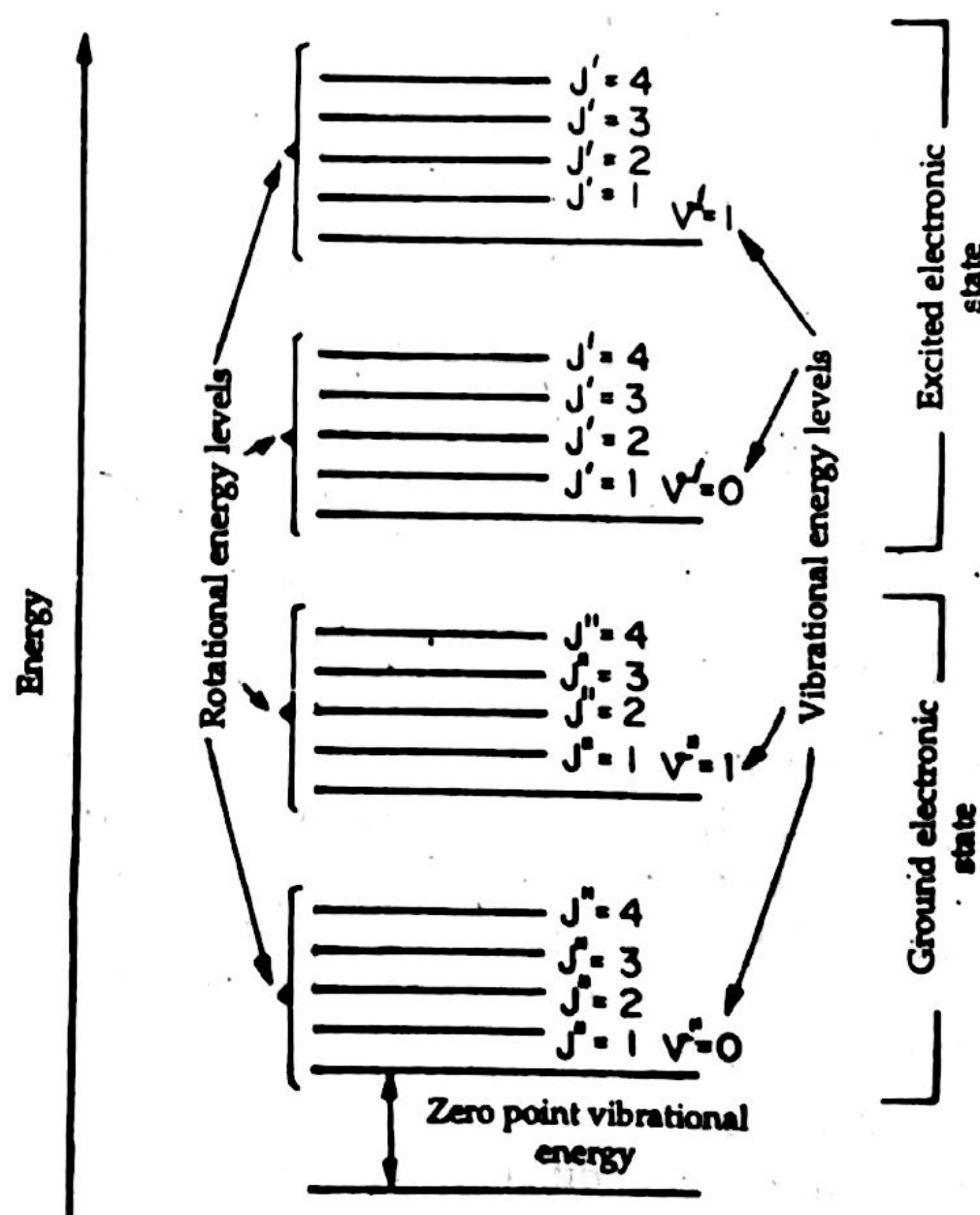


Fig. 3. Energy level diagram showing the various molecular energies.



It is to be noted that a series of rotational energy levels (designated by the rotational quantum number  $J$ ) are associated with each vibrational energy level (designated by the vibrational quantum number  $v$ ). And a series of vibrational energy levels are associated with each electronic state, Fig. 3.

**Table 1.** Summary of the various types of molecular spectra

S. No.	Spectra	Transitions	Region of electromagnetic spectrum	Criteria
1.	Rotational (or microwave)	between rotational energy levels	Microwave ( $1 - 100 \text{ cm}^{-1}$ )	Molecule must possess permanent dipole moment e.g. HCl, H <sub>2</sub> O etc.
2.	Vibrational & vibrational rotational (or infrared)	between vibrational energy levels	infrared ( $500 - 4000 \text{ cm}^{-1}$ )	Dipole moment of molecule must change during vibrations.
3.	Electronic (or UV-Visible)	between electronic energy levels	visible ( $12,500 - 25,000 \text{ cm}^{-1}$ ) and UV ( $25,000 - 70,000 \text{ cm}^{-1}$ )	Presence of chromophore in a molecule.
4.	Raman	between vibrational and rotational levels.	Far and near infrared regions	Periodic change in polarizability due to vibrational and rotational transitions.
5.	Nuclear Magnetic Resonance (NMR)	between magnetic energy levels of nuclei	Radio frequency	Spin quantum number of nuclei ( $I > 0$ )
6.	Electron spin Resonance (ESR)	between magnetic energy levels of unpaired electron(s)	Microwave	Presence of unpaired (or odd) electron in a molecule

## 2 INFRA-RED (OR VIBRATIONAL) SPECTROSCOPY

IR spectroscopy is an invaluable tool in organic structure determination and verification. It uses infrared (IR) radiation with frequencies between  $4000$  and  $400 \text{ cm}^{-1}$  (wave numbers). IR radiations can be utilized in organic structure determination by making use of the fact that it is absorbed by interatomic bonds in organic compounds. Chemical bonds in different environments will absorb varying intensities and at varying frequencies. Thus IR spectroscopy involves collecting absorption information and analyzing it in the form of a spectrum. The frequencies at which there are absorptions of IR radiation ("peaks" or "signals") can be correlated directly to bonds within the compound under investigation. As a general rule, the most important factors determining where a chemical bond will absorb are the bond order and the types of atoms joined by the bond.

- (i) Conjugation and nearby atoms shift the frequency to a lesser degree.
- (ii) The greater the masses of attached atoms, the lower the IR frequency at which the bond will absorb.

Therefore, the same or similar functional groups in different molecules will typically absorb within the same, specific frequency ranges. IR spectra can be used to provide information on the functional groups as well as the structure of a molecule as a whole.

IR spectra are commonly divided into following three regions :

~~(i)~~ *Functional group region*: It is the high frequency region, between  $4000 - 1300 \text{ cm}^{-1}$  (or  $2 - 7.7 \mu\text{m}$ ). This is because the characteristic stretching frequencies for important functional groups such as  $\text{C}=\text{O}$ ,  $\text{OH}$ , and  $\text{NH}$  occur in this region.

~~(ii)~~ *Finger print region*. It is the middle frequency region, between  $1300 - 900 \text{ cm}^{-1}$  (or  $7 - 11 \mu\text{m}$ ). In this region, complex absorptions occur due to combinations of interacting vibrational modes, providing a unique fingerprint for every molecule.

(iii) *Low-frequency region*. It is the region between  $900 - 650 \text{ cm}^{-1}$  (or  $11 - 15 \mu\text{m}$ ). It provides general classification of molecules from the pattern of absorption, such as substitution patterns on a benzene ring. The absence of absorptions in this region can provide a good evidence for the absence of an aromatic compound. Obtaining a broad, moderately intense absorption in this region indicates the presence of carboxylic dimers, amines, or amides.

#### ~~X~~ Information provided by infrared spectroscopy

(i) *"It can identify unknown materials"*. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material.

(ii) *"It can determine the amount of components in a mixture"*. The size of the peaks in the spectrum is a direct indication of the amount of material present.

(iii) *"It can also determine the quality or consistency of a sample"*.

#### Instrumentation of Infrared Spectrophotometer

Infrared spectrophotometer are either single beam or double beam.

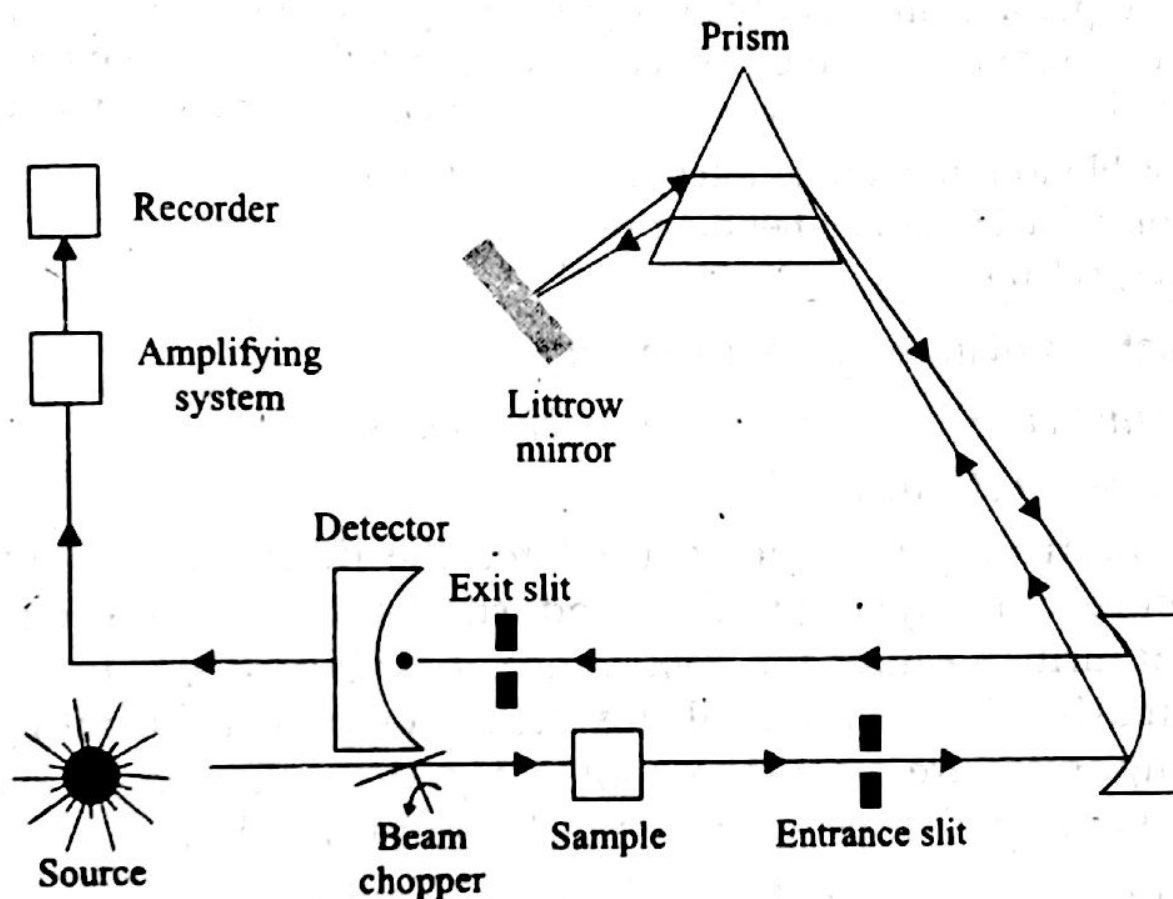
In the *single beam IR spectrometer*, the radiation emitted from the source are passed through a cell containing the sample and then through the prism which disperses the light. These instruments are simple, sensitive, accurate and versatile. However, these instruments have following disadvantages :

- (a) When the spectra of the solution is to be recorded, the absorption bands due to solvent are also obtained, making the analysis difficult.
- (b) The line obtained without the use of the sample in the light path (i.e., the base line) slopes because the intensity of the source changes continuously with the wavelength.

The *double beam spectrometers* are so designed that the light from the source is split into the beams of equal intensity, one passing through the sample and the other through the reference (air or solvent) for compensation. The two beams are recombined on to a common axis and are alternately focussed on to the entrance slit of the monochromator. This avoids the disadvantage (b) above and a horizontal base line is obtained.

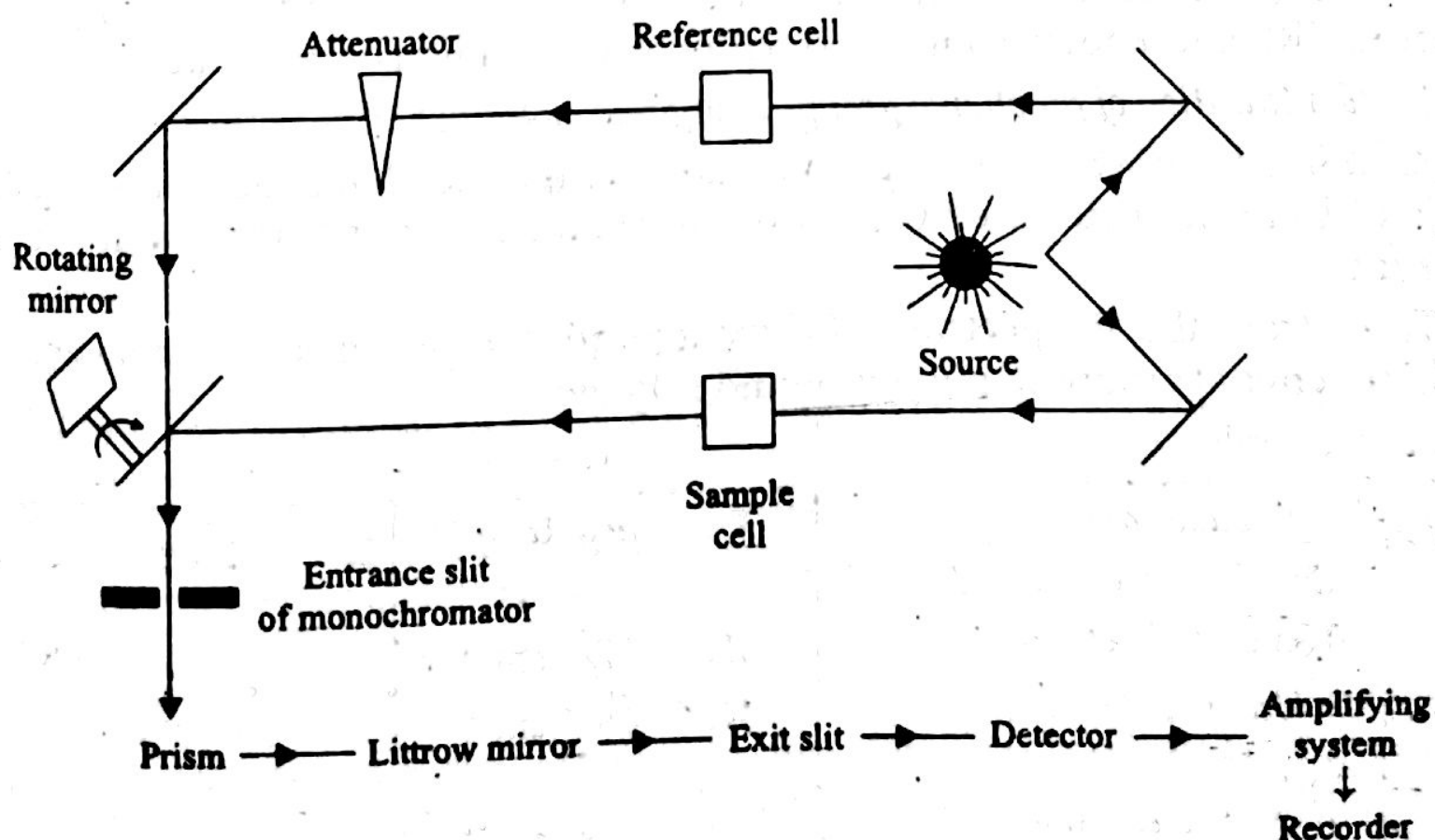
**Schematic diagrams for a typical IR spectrometer :**

**(i) Single-beam instrument**



**Fig. 4**

**(ii) Double beam instrument**



**Fig. 5**



## Differences between IR and UV spectrum

IR Spectrum	UV Spectrum
(i) IR radiation is used which causes bending and stretching vibrations in organic compounds.	UV radiation is used for getting UV spectrum. Electronic excitation takes place.
(ii) The IR spectra are usually expressed in terms of frequency in wave number units.	The UV spectra are generally expressed in terms of wavelength in nm units.
(iii) It helps especially in identifying the functional group of the organic compound.	It helps in confirming the presence of conjugated system and/or carbonyl group in the organic compound.
(iv) It is possible to differentiate inter-and intra-molecular Hydrogen-bonding by using IR spectrum.	Not possible.

## 2.1 Applications of Infrared Spectroscopy

~~(1)~~ Determination of force constant from vibrational spectrum.

(2) Determination of purity.

Infrared spectroscopy is widely used for the detection of impurities for production control of many chemicals on industrial scale. Whenever a compound is having an impurity it causes the appearance of extra bands, reduces the sharpness of individual bands and a general blurring of the spectrum. Conditions for the detection of impurities are most favourable when the main component does not possess strong bands in that IR region where the impurity shows.

For example, the small quantity of ketone in a hydrocarbon is detected by the appearance of a band near  $1720\text{ cm}^{-1}$ , which is a characteristic frequency of carbonyl group.

~~(3)~~ Identification of an unknown compound.

This is generally done by fingerprint technique which involves matching the spectrum (IR) of unknown compound with that of a known compound.

~~(4)~~ Identification of functional groups in organic molecules.

As different functional groups in organic compounds have the characteristic values of  $k$  and  $\mu$ , hence they will absorb at characteristic frequencies in the IR spectrum.

Thus, from the IR-spectrum of a compound, the presence and absence of certain functional groups in the compound is known.

For example :

S.No.	Functional Group	Frequency Range	Figure
(1)	C = O stretching vibration of (i) Saturated ketones (ii) Unsaturated ketones	$1705 - 1725\text{ cm}^{-1}$ $1665 - 1685\text{ cm}^{-1}$	Fig. 6
(2)	Alcohol (i) O - H stretching (ii) O - H bending	$3650 - 3590\text{ cm}^{-1}$ $1150 - 1050\text{ cm}^{-1}$	Fig. 7

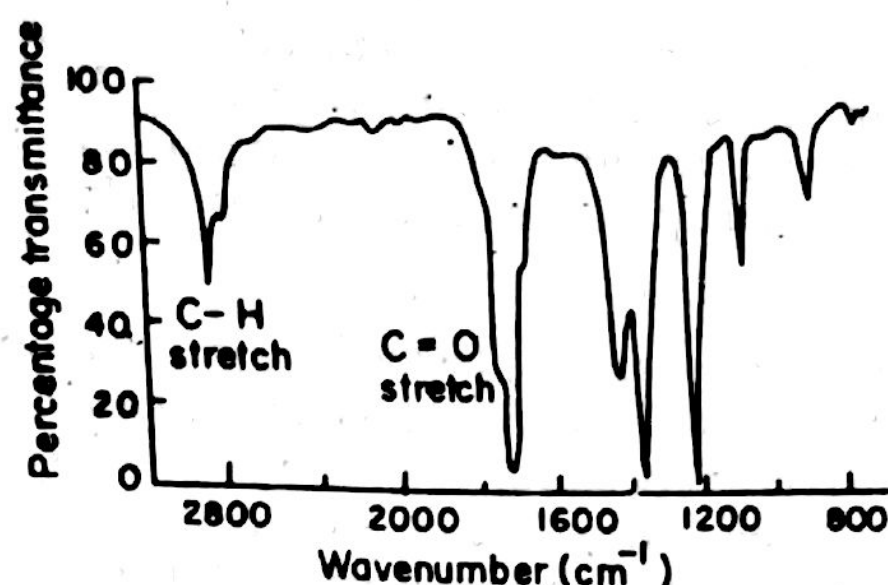


Fig. 6. IR spectrum of Dimethyl ketone.

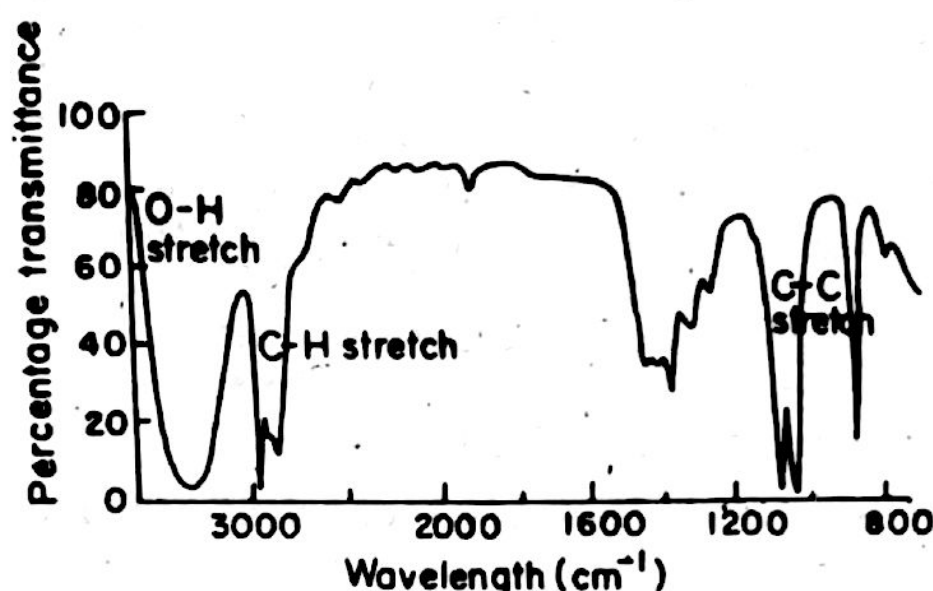


Fig. 7. IR spectrum of ethyl alcohol.

(5) *To distinguish between intra and inter molecular Hydrogen bonding.*

This can be done by taking a series of IR spectra of the compound at different concentrations. As the concentration is increased, the absorption band, due to intermolecular hydrogen bonding increases, while that due to intramolecular H-bonding remains unchanged. It is to be noted that O-H stretching for H-bonded alcohols appear at  $3550 - 3200 \text{ cm}^{-1}$ .

(6) *Elucidation of structure.*

Structure elucidation is possible by IR spectroscopy because it gives valuable information regarding molecular symmetry, dipole moments, bond lengths, bond strength etc.

### 3 ELECTRONIC (UV-VISIBLE) SPECTROSCOPY

It involves the transitions of electron(s) within a molecule or ion from a lower to a higher electronic energy level or vice-versa by the absorption or emission of radiations falling in the UV-visible range of electromagnetic spectrum.

While electronic spectra in the visible range span  $12,500 - 25,000 \text{ cm}^{-1}$ , those in the UV region span  $25,000 - 72,000 \text{ cm}^{-1}$ .

As the electronic energy levels are quantized. It means a discrete line should appear in the spectra for every transition. But a discrete line is not obtained since electronic transitions are accompanied by vibrational and rotational transitions. This leads to the appearance of bands in the electronic spectra of simple molecules in the gaseous phase.

An important principle for the interpretation of electronic spectra was given by Franck and Condon. According to this, positions and velocities of nuclei do not change during the electronic transitions which occur more quickly than the period of vibration of the nuclei as they are heavier compared to electron.

### UV-Vis Spectroscopy

UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at specific wavelength and applying the Lambert Beer's law.

Because the UV-Vis range spans the range of human visual acuity of approximately 400 – 750 nm, UV-Vis spectroscopy is useful to characterize the absorption, transmission and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters. This more qualitative application usually requires recording at least a portion of the UV-Vis spectrum for characterization of the optical or electronic properties of materials.

Ultraviolet/visible light : Wavelengths ( $\lambda$ ) between 190 and 800 nm.

### 3.1 Classifications of Electronic Transitions

Electronic transitions in molecules can be broadly classified into

- (i)  $\sigma \rightarrow \sigma^*$  Transition : As  $\sigma$  electrons are held more firmly in the molecule, this transition takes place in UV or far UV region.
- (ii)  $\pi \rightarrow \pi^*$  Transition : This transition takes place in the near UV and visible regions.
- (iii)  $n \rightarrow n^*$  Transition : These transitions are generally of weak intensities and lie in the visible region.

The relative energies of the molecular orbitals are illustrated below in Fig. 8 for mostly encountered organic compounds.

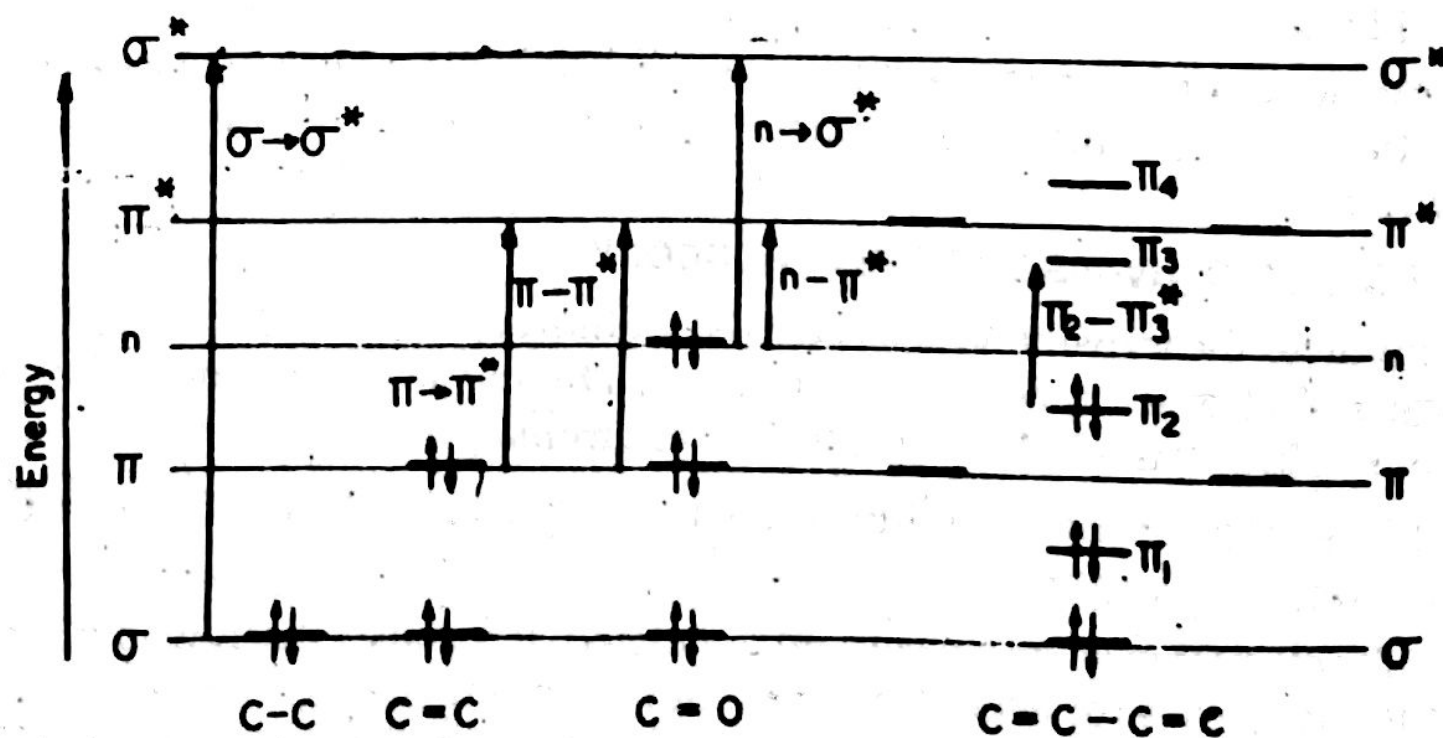


Fig. 8. Electronic Transitions and relative energies of molecular orbitals.



The positions of bands for different electronic transitions are summarized below :

Organic Compound	Electronic Transition	Position of band and Remarks
1. Alkanes	$\sigma \rightarrow \sigma^*$	(~ 150 nm) (Requires high energy which do not lie in UV region.)
2. Alkenes (simple)	$\pi \rightarrow \pi^*$	(170 – 190 nm)
3. Saturated aliphatic ketones	$n \rightarrow \pi^*$	(~ 280 nm) (Forbidden and hence of low intensity)
	$n \rightarrow \sigma^*$	(~ 185 nm) (Allowed and hence of high intensity)
	$\pi \rightarrow \pi^*$	(~ 160 nm) (Allowed and hence of high intensity)
4. Conjugated dienes	$\pi \rightarrow \pi^*$	(~ 217 nm) (Transition is of very low energy and is due to conjugation.)

### 3.2 The Chromophore concept

In Greek chromophore means colour carrier. Originally, a chromophore was any group which is responsible for imparting colour to the compounds. For example, Nitro group is a chromophore because it imparts yellow colour to nitro compounds. But these days, chromophore is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or the visible region, irrespective of the fact whether colour is produced or not.

#### Types of Chromophores

(i) Chromophores, which contains  $\pi$  – electrons and they undergo  $\pi \rightarrow \pi^*$  transition. For example, ethylenes, acetylenes etc.

(ii) Chromophores which contain both  $\pi$  and  $n$  electrons and they undergo  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions. For example, Carbonyls, nitriles etc.

**Auxochrome** is basically a colour enhancing group. It has the ability to extend the conjugation of the chromosphere by the sharing of the non-bonding electrons and thus shifts the absorption band towards the longer wavelength (the red end of the spectrum). Auxochrome by itself does not act as chromophore. Some common auxochrome groups are – OH, – OR, – NH<sub>2</sub>, – SH, etc.

### 3.3 Absorption and Intensity Shifts

(i) **Hypsochromic shift (or Effect)**. It leads to the shift of absorption maximum towards shorter wavelength. It is also known as Blue shift and is due to either the removal of conjugation or change in polarity of the solvent. For example, absorption maximum of aniline shifts from 280 m $\mu$  to 200 m $\mu$  in acidic solutions, which results

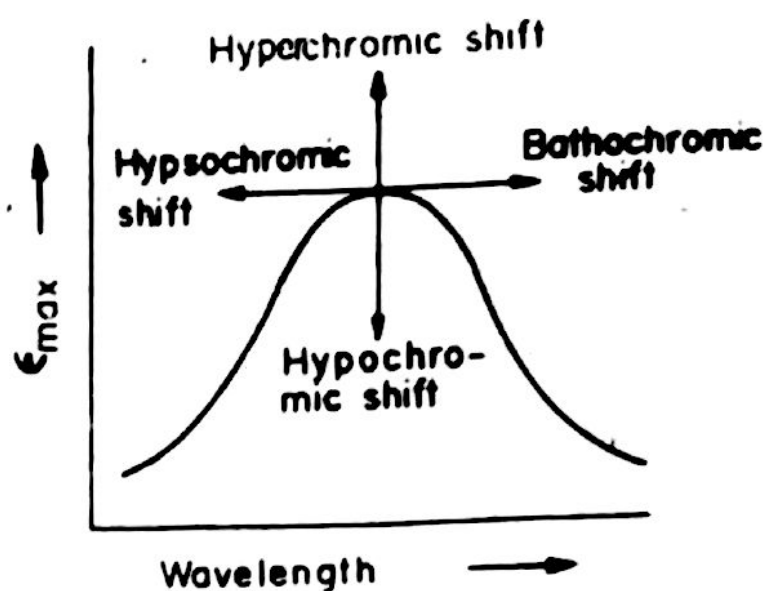
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in the formation of C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub> from C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> obviously, the lone pair is no longer present on – NH<sub>2</sub> group and hence conjugation is removed which results in blue shift.

(b) **Bathochromic shift (or effect)**. It leads to the shift of absorption maximum towards longer wavelength due to the presence of auxochrome. It is also known as red shift. It can also result by the change of solvent. For example, the  $n \rightarrow \pi^*$  transition for carbonyl compounds experience bathochromic shift when the polarity of the solvent is lowered.

(c) **Hyperchromic effect (or shift)**. It leads to the increased intensity of absorption.

(d) **Hypochromic effect (or shift)**. It leads to the decreased intensity of absorption.

Fig. 9. The various shifts in  $\epsilon_{\max}$  and  $\lambda_{\max}$ .

### 3.4 Applications of Electronic Spectroscopy

(i) For the characterization of aromatic compounds and conjugated dienes or other olefins.

(ii) Detection of impurities. For example, Benzene is the common impurity in cyclohexane and its presence can be easily detected by the absorption at 255 nm.

(iii) Control of purification. The process of purification should be continued till the compound which is being purified, stops showing bands due to impurity.

If the impurity does not absorb in the UV radiation, the purification procedure must be continued till  $E_{\max}$  corresponds to the 100% pure compound.

(iv) Determination of Unknown concentration. Since Absorbance (A) is given by

$$A = \epsilon C x$$

For a solution of some compound in the same sample cell  $\epsilon$  and  $x$  are constants.

Absorbance of standard solution ( $A_s$ ) and unknown solution ( $A_u$ ) is measured with the help of spectrophotometer. Knowing the value of concentration of standard solution ( $C_s$ ), concentration of unknown ( $C_u$ ) can be determined.

$$\text{Since } \frac{A_s}{C_s} = \frac{A_u}{C_u} \Rightarrow C_u = \frac{A_u}{A_s} \times C_s$$

(v) Determination of Molecular Weight. Molecular weight determination is possible provided suitable derivatives could be prepared which absorb in the UV visible range.

For example, Molecular weight of amine can be determined by first converting it into amine picrate. A known weight of it is dissolved per litre of solution and its absorbance is determined at  $\lambda_{\max}$ .

Since  $A = \epsilon C x$  hence  $C$  can be determined, which is in moles/L units. Since weight of amine picrate dissolved in 1L of solution is known so molecular weight of amine picrate and hence of amine can be determined.

(vi) Study of kinetics of chemical reaction. It is done by measuring the change in concentration of reactant or product with time provided one of the reactants or products exhibit suitable absorption in the UV-visible region. As absorbance is directly proportional to concentration, UV spectrophotometry can be used to follow the course of the reaction.



#### 4 NUCLEAR MAGNETIC RESONANCE (NMR)

It is a branch of spectroscopy in which radio frequency waves induce transitions between magnetic energy levels of nuclei of a molecule, which are created by keeping the nuclei in a magnetic field.

##### 4.1 NMR

Spectroscopy is the study of the interaction of electromagnetic radiation with matter.

Nuclear magnetic resonance spectroscopy is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter. As a consequence, NMR spectroscopy finds applications in following areas of science.

- (i) NMR spectroscopy is routinely used by chemists to study chemical structure using simple one-dimensional techniques.
- (ii) Two-dimensional techniques are used to determine the structure of more complicated molecules.
  - NMR is still the only method of determining the structure of a molecule in a liquid state and it challenges X-ray spectroscopy in the field of solid state structure analysis.
  - One and two-dimensional NMR techniques are replacing X-ray crystallography for the determination of protein structure.
- (iii) Time domain NMR spectroscopic techniques are used to probe molecular dynamics in solutions.
- (iv) Solid state NMR spectroscopy is used to determine the molecular structure of solids.
- (v) NMR methods have also been developed by scientists to measure diffusion coefficients.
- (vi) NMR is an applicable technique for organic chemistry, biochemistry, biomedicine, polymer chemistry, etc. because the most sensitive nucleus in NMR is proton *i.e.*, nuclei of a hydrogen atom.
- (vi) MR-imaging is another growing field of interest in NMR. The water content of the human body allows the making of proton charts or images of the whole body or certain tissues. Because static magnetic fields or radiopulses have been found not to injure living organisms, MR-imaging is competing with X-ray tomography as the main diagnostic tool in medicine.

##### Do You Know!

The Nobel prize has been awarded twice for work related to NMR.

1. F. Bloch and E.M. Purcell received the Nobel prize in Physics, in 1952, for the first experimental verifications of the phenomenon.
2. Prof. R.R. Ernst received the Nobel prize in Chemistry, in 1991, for the development of the NMR techniques.

##### Classification of NMR spectroscopy :

Modern NMR spectroscopy is frequently divided into several categories :

- (i) High power mode on highly relaxing nuclei which exhibit very broad lines, or polymers etc.



- (ii) The study of solids using for example magic angle spinning techniques.
- (iii) NMR 3D imaging to resolutions of  $\sim 1$  mm.
- (iv) High resolution mode on homogeneous solutions.

**The types of information accessible via high resolution NMR include :**

- (a) Functional group analysis (chemical shifts).
- (b) Bonding connectivity and orientation (J-coupling).
- (c) Through space connectivity (overhauser effect).
- (d) Molecular conformations, DNA, peptide and enzyme sequence and structure.
- (e) Chemical dynamics (lineshapes, relaxation phenomena).

### Theory of NMR

The nuclei with spin quantum number ( $I$ ) greater than zero can exhibit the NMR phenomenon. For example, proton has  $I = 1/2$ , so it can exhibit NMR commonly known as Proton magnetic resonance (PMR).

A magnetic nucleus can take  $(2I + 1)$  different orientations under the influence of an external magnetic field.

For example, proton (with  $I = 1/2$ ), can take  $2 \times 1/2 + 1 = 2$  orientations – either aligned or opposed to the field.

Proton is a spinning magnet since it has both electric charge and mechanical spin. Hence, it will precess around the axis of an applied external magnetic field. As explained above, precession can be in two principal orientations, either aligned with the external magnetic field ( $B_0$ ) or opposed to the field. These two orientations have low and high energy respectively.

The frequency of precession of proton ( $\nu$ ) is proportional to the strength of applied external field ( $B_0$ ) experienced by the proton.

$$\text{Quantitatively, } \nu = \gamma \frac{B_0}{2\pi}$$

where  $\gamma = \text{gyromagnetic ratio} = \frac{\text{nuclear magnetic moment } (\mu)}{\text{Nuclear angular momentum } (I)}$

### Precessional frequencies of proton as a function of increasing field strength

Magnetic flux density ( $B_0$ ) (Tesla)	1.4	2.3	4.7	14.1
Precessional frequency (MHz)	60	100	200	600

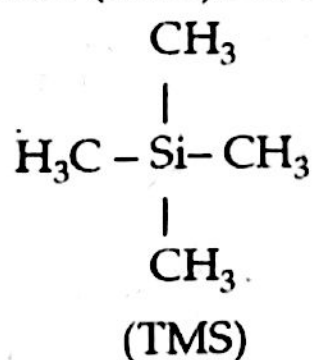
It is to be noted that magnetic moment ( $\mu$ ) determines the sensitivity of the NMR experiment and hence the strength of the signal. Fortunately,  $\mu$  of proton is large and hence it can be easily detected by NMR.

When a proton is precessing in the aligned orientations, it has low energy. When it is irradiated with a beam of correct frequency from radiofrequency source, it will absorb the energy, provided precessing frequency is the same as the frequency of the radiofrequency beam. (when this occurs, the radio frequency beam and the nucleus are in resonance, *that's why it is known as nuclear magnetic resonance*). After absorption of energy, proton will pass into higher energy state and starts precessing in opposite orientation. We record this absorption of energy in the form of an NMR spectrum. Subsequently it can lose this extra energy and relax back (either by spin-spin relaxation or spin-lattice relaxation) into the aligned position.

It is to be noted that all protons in a given molecule do not precess with the same frequency. Absorption depends upon the radio frequency which a particular proton feels. This in turn depends on the chemical environment of the proton. Thus at a given magnetic field different sets of chemically equivalent protons require slightly different frequency to cause absorption. Because the shift in frequency depends upon the chemical environment, it is called the *chemical shift*.

The electrons around the proton are induced to circulate in a magnetic field. These circulating electrons generate a small secondary magnetic field which acts diamagnetically (in opposition) to the applied field. The induced diamagnetic shielding effect is directly proportional to the electron density circulating around the nuclei. Hence greater the electron density, lower will be the precessional frequency of the proton. Using this, we can easily explain the fact that  $\text{CH}_3$  group in  $\text{CH}_3\text{F}$  comes to resonance at higher frequency than those of  $\text{CH}_3\text{Cl}$ . Since electronegativity of  $\text{F} > \text{Cl}$ , so fluorine withdraws electron density from the methyl group in  $\text{CH}_3\text{F}$  to a greater extent than  $\text{Cl}$  in  $\text{CH}_3\text{Cl}$ . Due to this deshielding effect, protons of methyl group experience a greater net magnetic field and hence precess with higher frequency.

Precessional frequency of a group of nuclei are measured w.r.t some reference group of nuclei like *tetramethyl silane (TMS)* in PMR.



TMS has 12 protons in magnetically equivalent positions so it gives intense sharp signal even at low concentrations.

Due to the +I effect of Si, Silicon pushes electrons into the methyl groups of TMS. Due to the greater electron density, TMS protons come to resonance at low frequency (defined as zero). In other words, precessional frequency of TMS protons is zero due to the powerful shielding effect.

TMS has low boiling point so it can be easily removed from recoverable sample of an organic compound. It is chemically inert and soluble in organic solvents.

TMS is used as an internal standard and is added to 0.01 to 1 percent to the sample solution for the measurement of differences in frequency w.r.t to it.

#### 4.2 Units used in NMR Spectroscopy and Appearance of NMR Spectra

*Delta ( $\delta$ ) units* are generally used for expressing chemical shift positions. These are defined as proportional differences from TMS as reference standard, in parts per million (ppm).

Let operating frequency of the instrument =  $\nu_0$  ppm

Frequency of TMS =  $\nu_{\text{TMS}}$  Hz

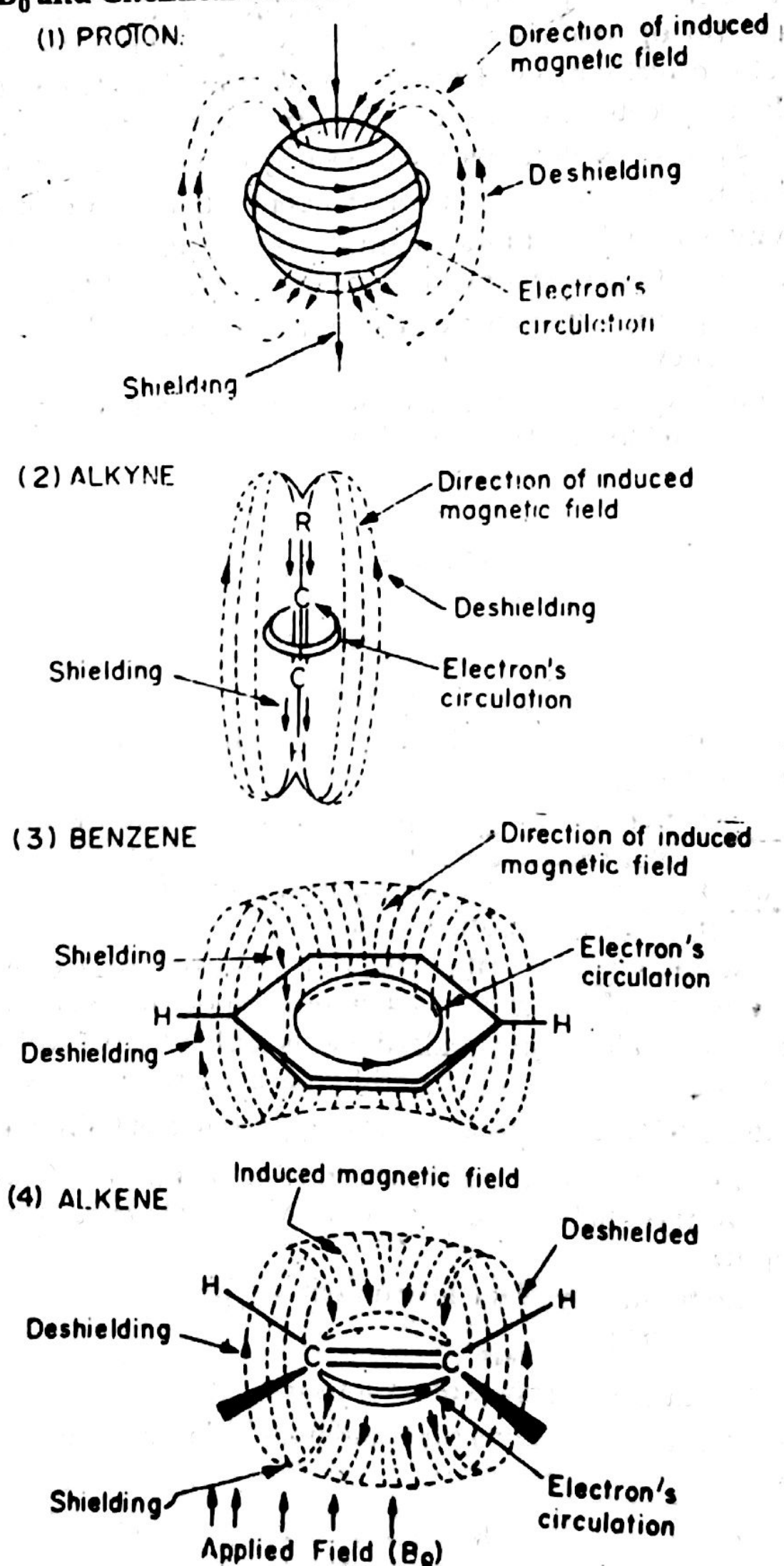
Frequency of unknown group of protons =  $\nu_u$  Hz

Then, chemical shift positions (in  $\delta$  units) for unknown group of protons in a given molecule

$$(\delta \text{ u}) = \frac{\nu_u - \nu_{\text{TMS}}}{\nu_0}$$

Generally, chemical shifts have  $\delta$  value 0 to 10. NMR signal is usually plotted with magnetic field strength ( $B_0$ ) decreasing to the left (down field). Greater the shielding of protons, smaller will be the value of  $\delta$  and the signal for TMS appears at extreme right of the spectrum with  $\delta = 0$  at high magnetic field strength (up field) or low frequency (low  $\nu$ ).

**Structure of Molecules and Direction of Induced Magnetic Field w.r.t. Direction of  $B_0$  and Chemical Shift Positions**



**Fig. 10.** Shielding and deshielding associated with Protons of different molecules.

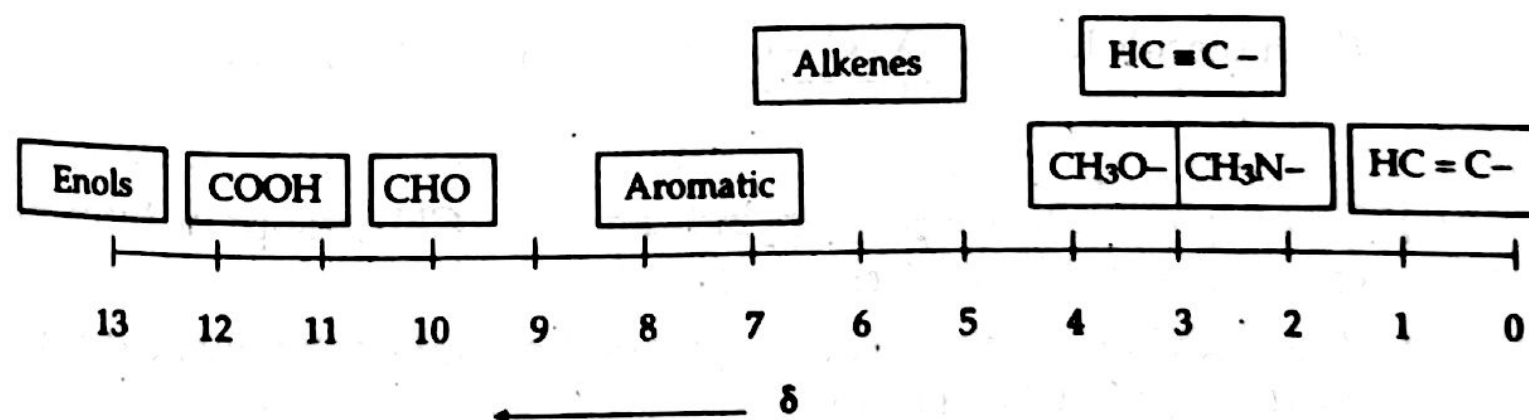


Protons which lie in the shielding zone, experience lower values of field so appear at low  $\delta$  value in the spectrum and require high field strength for resonance to take place. For example, Acetylenic protons.

In contrast, protons which lie in the de-shielded zone, appear at high  $\delta$  value. For example, aromatic protons.

**Table. 2 : Values of Protons in Organic Compound**

Compound	$\delta$ - value	Compound	$\delta$ - value
Tetramethylsilane	0.00	Dioxane	2.8
Cyclopropane	0.22	Nitromethane	4.28
Methane	0.23	Water	5.2
Tetramethylmethane	0.92	Methylene chloride	5.8
Ethyl alcohol			
Methyl protons	1.17	Ethylene	5.84
Methylene protons	3.59	Benzene	7.27
Cyclohexane	1.44,		
Methyl cyanide	1.97	Chloroform	7.7
Acetone	2.09	Naphthalene	7.73
Acetaldehyde			
Methyl protons	2.15		
Aldehydic proton	9.72		
Methyl alcohol			
Methyl protons	3.38		



**Fig. 11. Approximate chemical shift positions for protons in organic molecules.**

#### 4.3 Interpretation of NMR Spectra

The number of signals in NMR tells us how many *different environments* are there in a molecule.

The area under each NMR signal is proportional to the number of hydrogen atoms in that environment. Thus, the relative areas of different peaks corresponds to number of protons present in different environments.

The multiplicity (or the number) of lines in NMR signal for a group of protons tells which atoms are present in neighbouring groups. If there are  $n$  neighbouring protons, then multiplicity of the signal is  $(n + 1)$ . Hence, for finding the multiplicity of the signal from a group of protons, count the number of neighbouring protons ( $n$ ) and add one.

When a group of protons have different chemical environments on either side then multiplet consisting of  $(n + 1)(n' + 1)$  lines is observed. Here  $n$  and  $n'$  are number of protons on one and the other side of particular group under study.

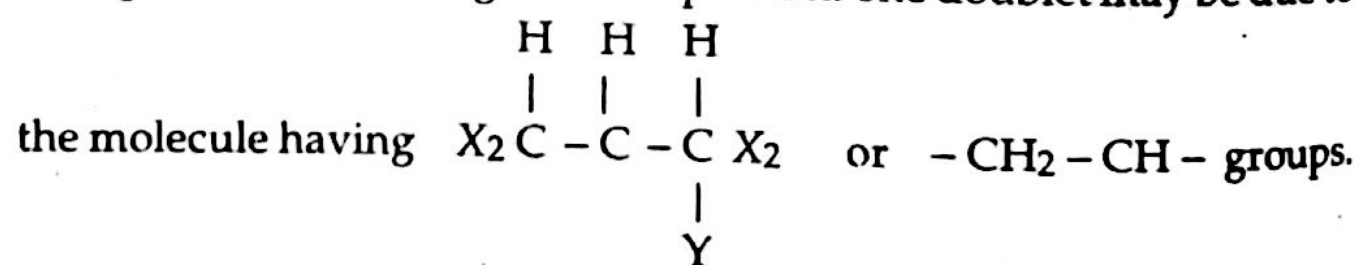
The relative intensities of different signals can be obtained with the help of pascal's triangle given below.

Neighbouring protons ( $n$ )	Number of signals ( $n + 1$ )	Relative intensities of signals
0	1	1
1	2	1 1
2	3	1 2 1
3	4	1 3 3 1
4	5	1 4 6 4 1
5	6	1 5 10 10 5 1
6	7	1 6 15 20 15 6 1

Let us consider few cases.

- (a) When NMR spectrum shows two signals, only singlets. It can be interpreted as two kinds of protons are there which are not on adjacent carbon atom (otherwise splitting might have occurred.)

- (b) The spectrum consisting of one triplet and one doublet may be due to



- (c) Two triplets in NMR spectrum indicate two  $-\text{CH}_2$  groups in different environments like  $\text{Y} - \text{CH}_2 - \text{CH}_2 - \text{X}$

- (d) When NMR spectrum shows septet and a doublet, it may be due to the  $(\text{CH}_3)_2\text{C} - \text{CH} -$  group.

- (e) When NMR spectrum shows two peaks with relative area 5:3, it means 5 and 3 protons are there in two different environments.

**Example 1.** Predict the NMR spectrum of  $\text{CH}_2\text{Cl} - \text{CHCl}_2$ .

**Solution.**  $\text{CH}_2\text{Cl} - \text{CHCl}_2$  has two sets of equivalent protons.

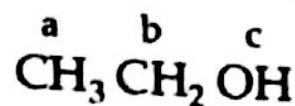
So, number of signals = 2.

For protons 'a',  $n = 1$  so doublet at upfield

For protons 'b',  $n = 2$  so triplet at down field.

**Example 2.** Predict the NMR spectrum of  $\text{CH}_3\text{CH}_2\text{OH}$ .

**Solution.**  $\text{CH}_3\text{CH}_2\text{OH}$  has three kinds of protons viz.



for protons *a*,  $n = 2$  so triplet is observed due to coupling with  $-\text{CH}_2-$  group at downfield.

For protons *b*,  $n = 3$  and  $n' = 1$ , so  $(3 + 1)(1 + 1) = 8$  lines multiplet is observed at in between.

For proton *c*,  $n = 2$  so triplet is observed due to coupling with  $-\text{CH}_2-$  gp at up-field.

**Example 3.** From the PMR spectrum of the compound  $\text{C}_3\text{H}_5\text{ON}$  in an acidic medium, suggest its structure. Given that the peak 1 disappears in the presence of  $\text{D}_2\text{O}$ .

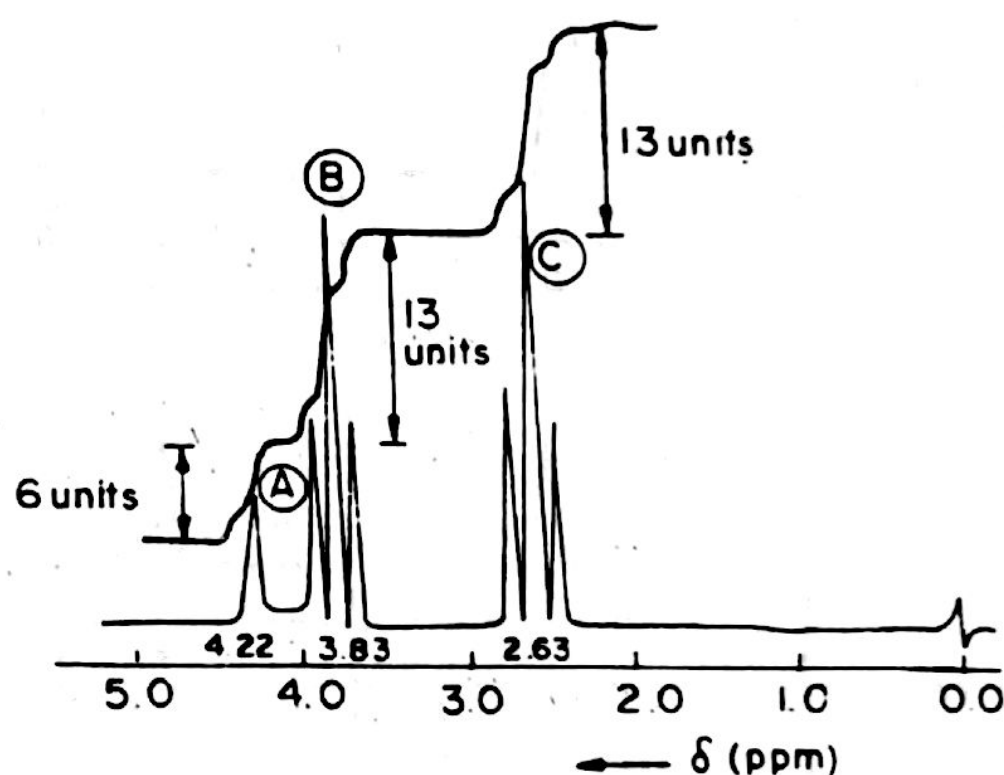


Fig. 12.

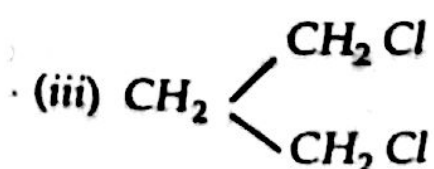
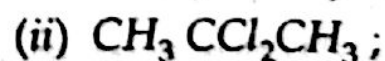
**Solution.** Since the peak (A) disappears in the presence of  $\text{D}_2\text{O}$ , it may be hydroxyl group.

The peaks (B) and (C) must represent the hydrogen atoms attached to the methylene group.

The analysis of integral trace indicates the presence of 1, 2 and 2 protons within the peaks A, B, C respectively.

Hence, two methylene groups attached to each other must be present, so structure is  $\text{HOCH}_2\text{CH}_2\text{CN}$ .

**Example 4.** Draw the low and high resolution spectra of:





Solution.

Sr.No	Molecule	Low resolution spectra	High resolution spectra
1	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH} \begin{array}{l} \diagup \text{Cl} \\ \diagdown \text{Cl} \end{array} \end{array}$	<p style="text-align: center;"><math>\delta</math> (ppm)</p>	<p style="text-align: center;"><math>\delta</math> (ppm)</p>
2	$\begin{array}{c} \text{Cl} \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{Cl} \end{array}$	<p style="text-align: center;"><math>\delta</math> (ppm)</p>	<p style="text-align: center;"><math>\delta</math> (ppm)</p>
3	$\begin{array}{c} \text{CH}_2 \begin{array}{l} \diagup \text{CH}_2\text{Cl} \\ \diagdown \text{CH}_2\text{Cl} \end{array} \end{array}$	<p style="text-align: center;"><math>\delta</math> (ppm)</p>	<p style="text-align: center;"><math>\delta</math> (ppm)</p>
4	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2 \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$	<p style="text-align: center;"><math>\delta</math> (ppm)</p>	<p style="text-align: center;"><math>\delta</math> (ppm)</p>

Fig. 13.

## 5 SPECTROPHOTOMETRY

When radiations are passed through a transparent layer of a sample (solid, liquid, or gas), certain characteristic wavelengths are removed by the process of absorption. The absorbed energy of the electromagnetic radiations is transferred to the atoms or molecules of the sample, thereby these get excited from the ground state to the excited state. The measurement of this decrease in the intensity of radiation is the basis of *Spectrophotometry*.

*Spectrophotometer* is an instrument used for absorption measurements. It can be made to operate in the ultraviolet, visible and infrared regions, using suitable source of radiant energy.

**Spectrophotometer has the following components :**

(i) **Source of electromagnetic radiation.** It is different for different spectroscopic techniques viz.

Spectroscopy	UV	Visible	IR	Microwave
Source	Hydrogen discharge lamp	Tungsten filament lamp	Electrically heated rod of rare-earth oxides (IR)	Klystron valve
Sample form	Gas or dilute solution	Gas or dilute solution	Gas or liquid or dilute solution or (Solid +KBr) in the form of disc	Gas or vapour

(ii) **Wavelength controller.** Wavelength can be controlled by using colour filter, light filter, prism, monochromator etc.

(iii) **Sample holder.** It can be test-tube in calorimetry, quartz cell in UV and visible spectroscopy etc.

(iv) **Photodetector and Receptor unit.** This unit detects and converts radiant energy into measurable electrical signal.

(v) **Amplification and Recording unit.** In this, amplification of electrical signal is done followed by output generation either on computer monitor or graphical print-out.

Spectrophotometer can be single beam or double-beam instruments. In double-beam spectrophotometers, a beam of light is split into two identical halves, known as sample beam and reference beam respectively. Sample beam is directed through a transparent cell containing a solution of the compound being analyzed.

Reference beam is directed through an identical cell that contain only the solvent. The instrument can compare the intensities of the two beams at each wavelength of the chosen region.

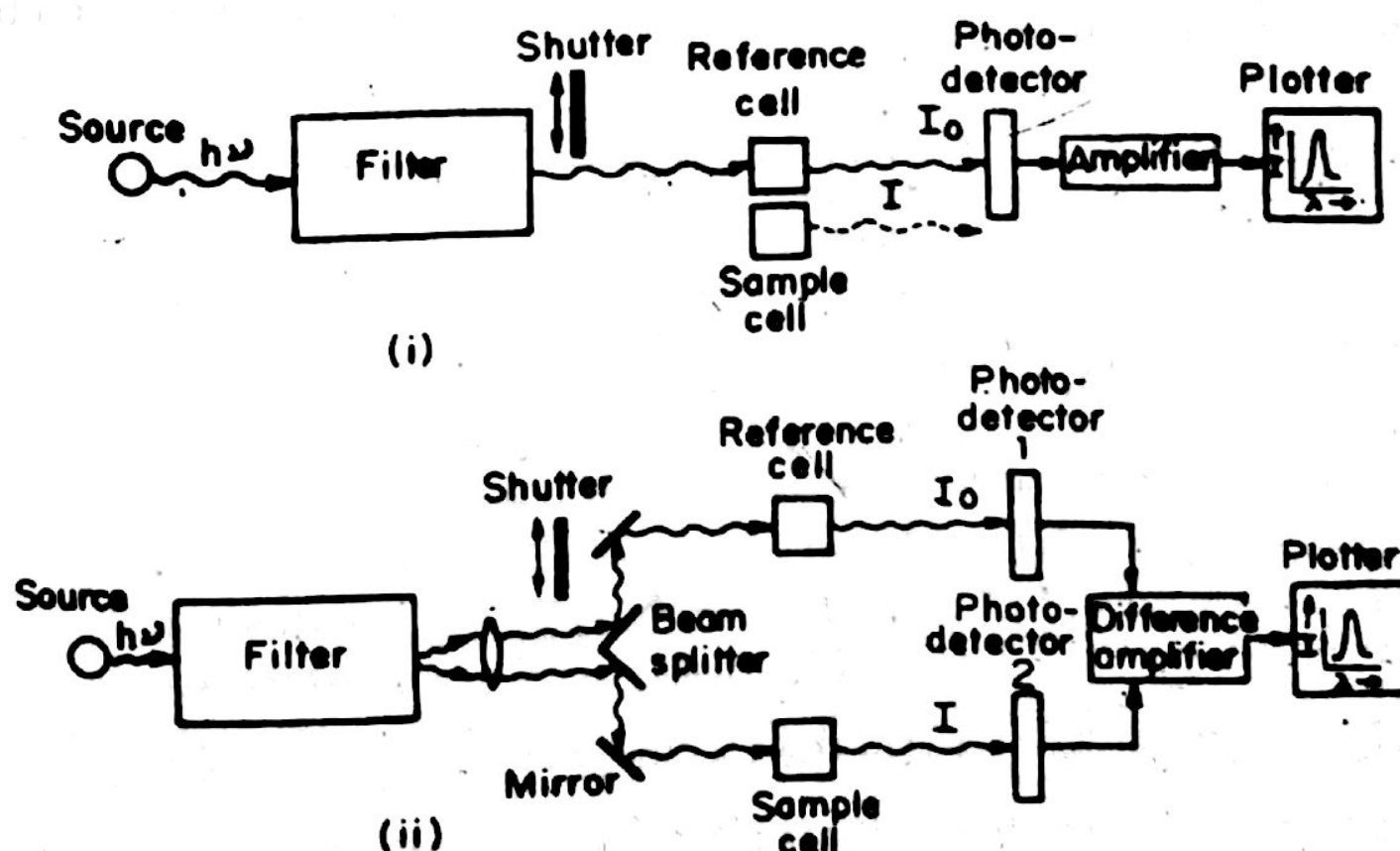


Fig. 14. (i) Single & (ii) Double beam spectrophotometers.

Suppose a sample absorbs light at a particular wavelength, then intensity of the sample beam ( $I$ ) will be less than of the reference beam ( $I_0$ ). Absorbance ( $A$ ) is  $\log(I_0/I)$ . Recording unit generates a graph between the wavelength of the entire region vs. the absorbance ( $A$ ) of the light at each wavelength.

The single largest application of the spectrophotometer is for **quantitative analysis**. The prerequisite for such analysis is a known absorption spectrum of the compound under investigation. The **absorption spectrum** is referred to as the wavelength of maximum absorption ( $A_{\max}$ ) which can be obtained by plotting absorbance vs. wavelength at a constant concentration of a given compound (see Fig. 15).

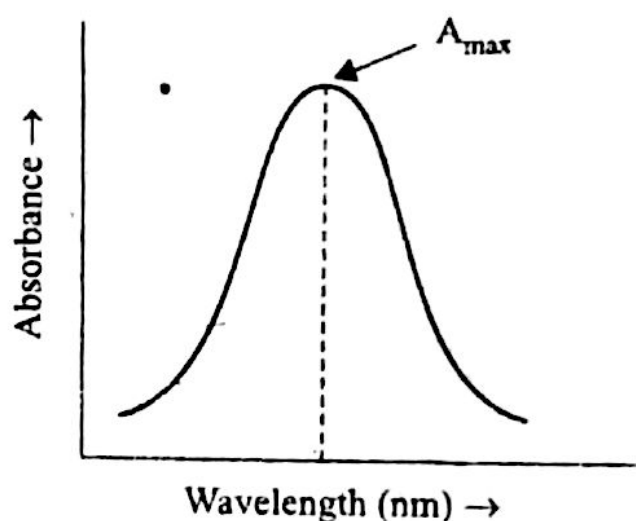


Fig. 15. Determination of absorbance spectrum.

Once the absorption spectrum is known, an unknown concentration of such a compound can be determined by measuring absorbance at its absorption maximum ( $A_{\max}$ ). This is usually done by (i) preparing a series of different concentrations of a given compound, (ii) Measuring their absorbance values at  $A_{\max}$  and (iii) Plotting absorbance vs. concentration to construct a **concentration curve**.

The concentration of the unknown sample can be located by drawing a straight line from point of absorbance of the unknown until it intersects with concentration curve, and then draw perpendicularly to the x-axis to identify the concentration of your unknown sample (see Fig. 16).

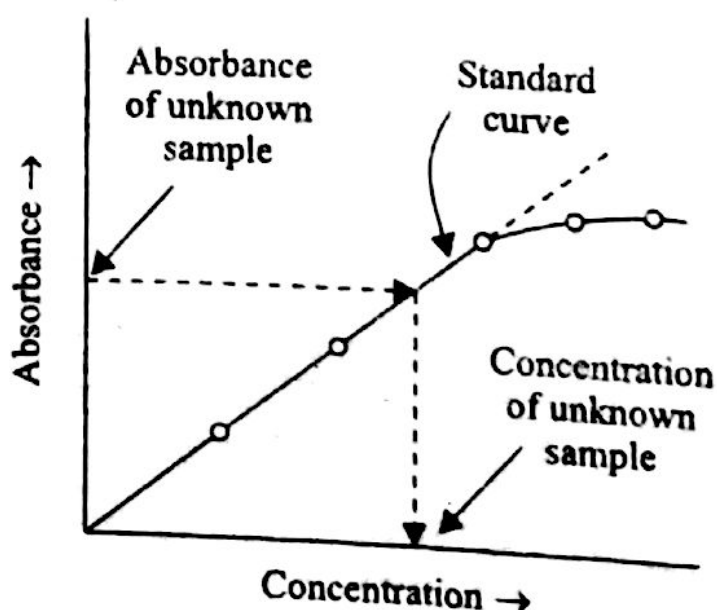


Fig. 16. Determination of unknown sample concentration using a standard curve.

It is obvious from the figure that only those points in the linear range of the standard curve should be used for accurate concentration determination.



The spectrophotometer can also be a useful tool for study of reaction rates and kinetics. Many enzymatic reactions can be followed by measurement of the rate of appearance or disappearance of light-absorbing (U.V. or visible) reactant or products as a function of time.

Spectrophotometer can also be used to determine the concentration of substance which do not absorb light at any of the wavelengths investigated. This is done by preparing suitable light absorbing derivatives of the substances or by employing an appropriate chromogen. The absorption of the coloured product formed is proportional to the concentration of the substances under investigation.

## 6 COLORIMETRY

The variation of the colour of the system with concentration is the basis of colorimetry. Colorimetric analysis is specially useful for systems in which substances or their solutions are colored. When a substance is colorless, then a suitable complexing agent is added to the solution so that a colored complex is obtained. The latter then absorbs light in the visible region. For instance, for the estimation of cuprous ions, complexing agent, ammonium hydroxide, is used to get blue coloured solution.

The working of a colorimeter can be explained with the help of block diagram as shown in Fig. 17 below :

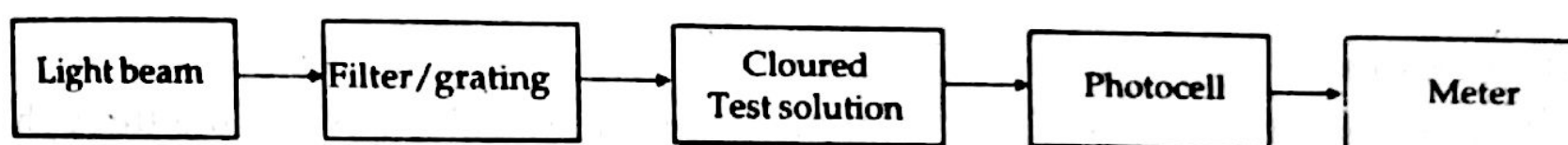


Fig. 17. Block diagram of colorimeter.

Colorimeters are provided with arrangements to select appropriate wavelength of light with the help of filter & grating. A light of proper wavelength is allowed to pass through a coloured test solution. The light transmitted from this solution is made to pass through photocell and proportional to the amount of light transmitted by solution, a current is generated in the photocell. A meter is calibrated to show the fraction of light absorbed which is proportional to the concentration of the coloured substance in test solution. From the measurements, concentrations of coloured solution can be obtained by using Lambert – Beer law.

### Important Factors

The most important idea in colorimetry is that color intensity is proportional to the concentration. However, this is not always true, especially at high concentrations and colour intensities.

Following factors are to be kept in mind when working with colorimetry :

- (i) What colors are absorbed and how intensely they are absorbed by depends on the chemical being used and how the electrons and energy levels within it are arranged.
- (ii) The color we see is complementary to the colour absorbed by the chemical.
- (iii) The mechanism is that "as light passes through a solution, light of a certain wavelength is absorbed by the coloured chemical specie".

- (iv) The assumption is that "the amount of light absorbed is directly proportional to the concentration of the chemical specie that the light passes through".
- (v) Also, the amount of light absorbed is directly proportional to the thickness (or path length) of the solution.
- (vi) These factors and assumptions can be summarized as **Beer's law** and written as the equation,  $A = abc$ . In this equation  $A$  is absorbance,  $a$  is a proportionality factor called the molar absorptivity,  $b$  is the path length, and  $c$  is the molar concentration.

### To sum up,

In colorimetry, the intensity of the color is measured and related to the concentration of the solution. This is useful and often used way of determining the concentration of a chemical in a solution, if it has a colour.

## 7 Beer's Law

It states that for a parallel beam of monochromatic radiation passing through homogeneous solutions of equal pathlength, the absorbance is proportional to the concentration.

i.e., for solutions 1 and 2

$$\frac{\text{Absorbance 1}}{\text{Absorbance 2}} = \frac{\text{Concentration 1}}{\text{Concentration 2}}$$

## Lambert's Law

It states that for a parallel beam of monochromatic radiation passing through homogeneous solutions of equal concentration, the absorbance is proportional to the path length.

i.e., for path lengths  $x$  and  $y$

$$\frac{\text{Absorbance } x}{\text{Absorbance } y} = \frac{\text{Path-length } x}{\text{Path-length } y}$$

## The Lambert-Beer's Law

It states that for a parallel beam of monochromatic radiation passing through a homogeneous solution the absorbance is proportional to the product of the concentration and path-length.

i.e., Absorbance ( $A$ )  $\propto$  Concentration ( $C$ )  $\times$  path-length ( $b$ )

$\Rightarrow$

$$A \propto bc$$

or

$$A = abc$$

where  $a$  is proportionality constant. Its value depends on the substance, the solvent, the wavelength and the units used for concentration and path-length.

Two common methods of expressing the constant are  $A$  (1%, 1 cm) and molar absorptivity.

(i)  $A$  (1%, 1 cm) is the absorbance of a 1 cm layer of a 1% weight by volume solution,

i.e., 
$$A = A(1\%, 1\text{ cm}) \times C \times L$$

where  $C$  is the concentration as % weight/volume and  $L$  is the path-length in cm.

$A$  (1%, 1 cm) values are generally found in the pharmaceutical literature.

(ii) Molar absorptivity ( $\epsilon$ ) for a specific wave-length is the absorbance of a 1 cm layer of a 1 mole/litre solution.

$$A = \epsilon \times C \times L$$

where  $C$  is the concentration in mole/litre and  $L$  is the pathlength in cm.

Molar absorptivities are found in the chemical literature.

According to the Lambert-Beer's law, there exists a linear relationship between absorbance and concentration of a solute when path length through the cell containing the solute is constant.

(In most standard spectrophotometers, the sample cell has a 1 cm path-length).

A plot of  $\log(I_0/I)$  or  $A$  vs. concentration of absorbing solute yields a straight line passing through the origin indicating conformity to the Lambert-Beer's law. However, this is valid only over a given range of solute concentrations with a value of  $\log(I_0/I)$  less than 1.

Note.  $I_0$  and  $I$  are the intensities of incident and transmitted light respectively.

The term transmittance ( $T$ ) is the ratio of the intensity of the light transmitted by a sample ( $I$ ) to the intensity of light incident on the sample ( $I_0$ ).

Thus,

$$T = I/I_0$$

Moreover,  $\%T = T \times 100 = I/I_0 \times 100$

The logarithm of the reciprocal of the transmittance [ $\log(I_0/I)$ , or  $\log(1/T)$ ] is termed absorbance ( $A$ ).

$$A = \log(1/T)$$

It should be noted that a plot of  $\%T$  vs. concentration of solute will not yield a straight line.

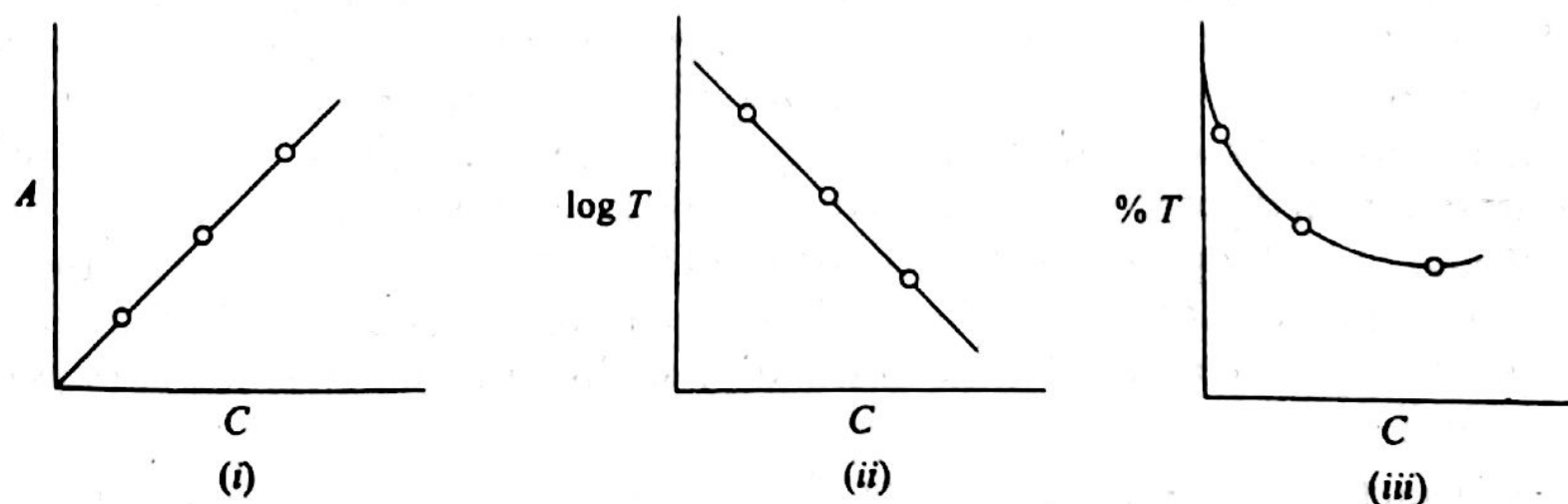


Fig. 18. Plots of  $A$  (i),  $\log T$  (ii) and  $\%T$  (iii) vs. concentration.

If multiple species that absorb light at a given wavelength are present in a sample, the total absorbance at that wavelength is the sum due to all absorbers:

$$A = (\epsilon_1 \times C_1 \times L) + (\epsilon_2 \times C_2 \times L) + \dots$$

where the subscripts refer to the molar absorptivity and concentration of the different absorbing species that are present.



**Limitations of the Lambert-Beer's Law :**

The linearity of the Lambert-Beer's law is limited by chemical and instrumental factors.

Causes of nonlinearity include :

- (i) Scattering of light due to particulates in the sample.
- (ii) Fluorescence or phosphorescence of the sample.
- (iii) Changes in refractive index at high analyte concentration.
- (iv) Shifts in chemical equilibria as a function of concentration.
- (v) Deviations in absorptivity coefficients at high concentrations ( $> 0.01$  M) due to electrostatic interactions between molecules in close proximity.
- (vi) Non-monochromatic radiation.

**8 CHROMATOGRAPHY – GAS CHROMATOGRAPHY****8.1 Introduction**

In 1903, Tswett used the term chromatography to describe the separation of plant pigments by percolating a petroleum ether extract through a glass column packed with powdered calcium carbonate. The various pigments migrated through the column at different rates & produced different coloured zones. Extrusion, followed by sectioning of the calcium carbonate packing led to the separation of the components.

The more complex, modern chromatographic techniques are used for a wide variety of separations frequently involving colourless substances, but the original term is retained.

“Chromatography is an analytical technique for identification, separation and purification of components of a mixture on the basis of difference in their affinity for stationary and mobile phases”.

Chromatography involves two mutually immiscible phases (*viz.*, stationary & mobile phases) which are brought into contact. A sample to be analyzed is introduced into a mobile phase. It is then carried along through a stationary phase packed in the form of column or thin-layer. Different constituents of the sample undergo repeated partitions between the mobile phase & the stationary phase. This results in gradual separation of constituents of the sample into bands in the mobile phase. Due to the wide choice of materials for the stationary & mobile phases, it is possible to separate molecules that differ only slightly in their chemical & physical properties.

In practice the liquid stationary phase is coated onto an inert powdered or granular solid support which is either spread on a supporting sheet in the form of a thin layer or packed into a column. In contrast, if the stationary phase is so it has no need of support if packed into a column but still requires a supporting sheet for thin layer operation.

Variation in the rate at which different constituents of mixture sample migrate through a stationary phase under the influence of a mobile phase (because of differences in distributions) is the basic principle of all the chromatographic techniques.

The need to separate and purify a product from a complex mixture is a necessary and important step in the production line of any chemical, drug or bioprocessing industry. Chromatography is a very special separation process because

- (i) It can separate complex mixtures with great precision. Even very similar components, such as proteins that may only vary by a single amino acid, can be separated with chromatography. In fact, chromatography can purify basically any soluble or volatile substance if the right absorbent material, carrier fluid, and operating conditions are employed.
- (ii) It can be used to separate delicate products because the conditions under which it is performed are not typically severe.

For these reasons, chromatography is so special. It works like magic and is quite well suited to a variety of uses in the field of biotechnology, such as separating mixtures of proteins.

### **Basic Operation of Chromatography**

Let's see what actually takes place in a chromatographic separation.

The process of a chromatographic separation takes place within a **chromatography column**. This column, made of glass or metal, is either a packed bed or open tubular column. [A **packed bed column** is comprised of a stationary phase which is in granular form and packed into the column as a homogeneous bed. The stationary phase completely fills the column. *Open tubular columns* are lined with a thin film stationary phase. The centre of the column is hollow so there is a passageway through the centre of the column.]

The *mobile phase* is typically a solvent moving through the column. It carries the mixture to be separated. It can be a liquid or a gas, depending on the type of process. The **stationary phase** is the material in the column for which the components to be separated have varying affinities.

The materials which comprise the mobile and stationary phases vary depending on the general type of chromatographic process being performed.

### **Gas Chromatography**

An inert gas is generally the mobile phase in gas chromatography. The stationary phase is generally an adsorbent or liquid distributed over the surface of a porous, inert support.

### **Liquid Chromatography**

The mobile phase in liquid chromatography is a liquid of low viscosity which flows through the stationary phase bed.

In any case, the partitioning of solute between the stationary and mobile phases lead to the desired separations.

(i) **Feed injection.** The feed (i.e., mixture to be separated) is injected into the mobile phase. The mobile phase flows through the system by the action of a pump.

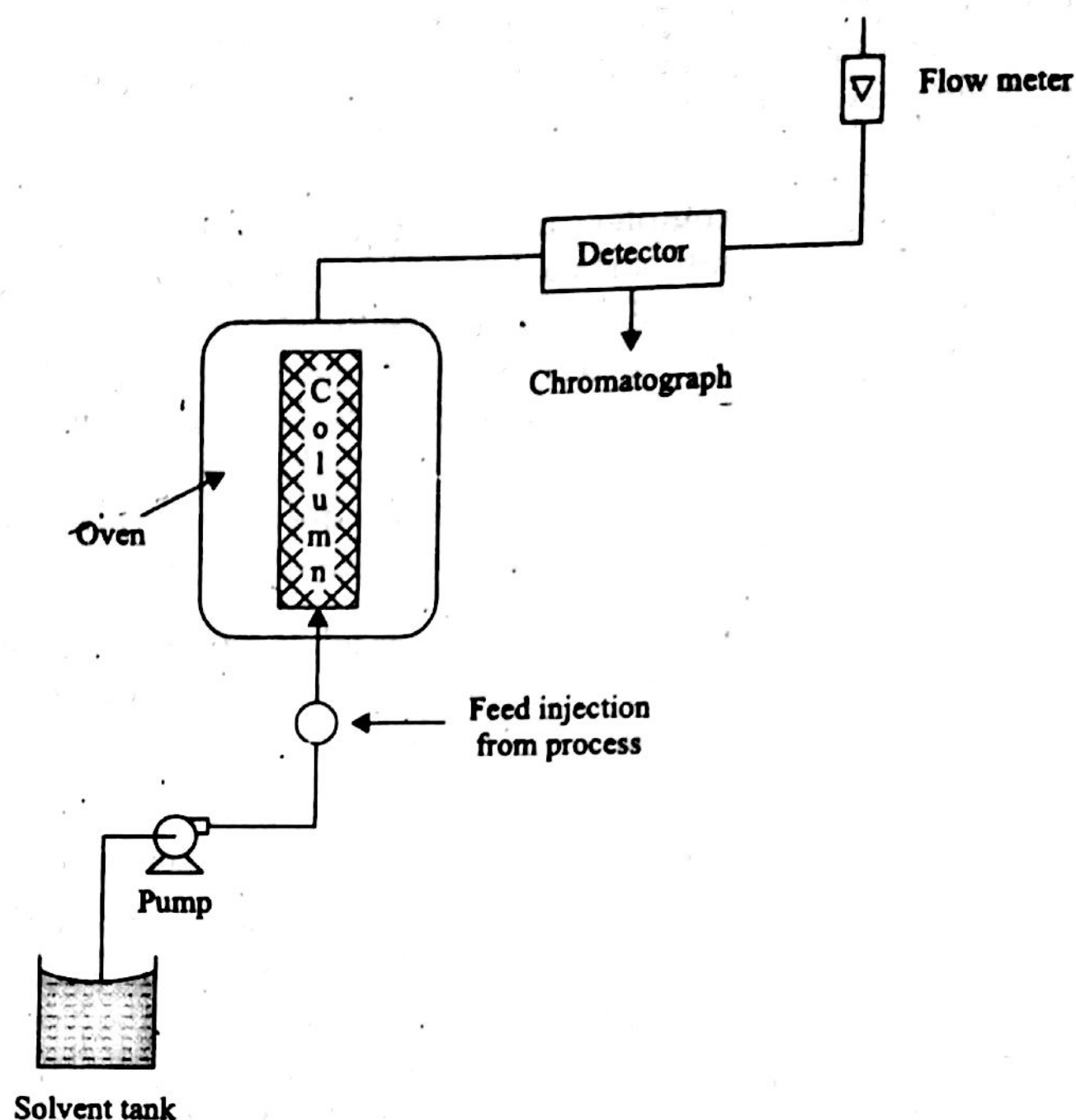


Fig. 19. Basic layout for chromatography operation.

(ii) **Separation in the column.** As the sample flows through the column, its different components will adsorb to the stationary phase to varying degrees. Those with weak attraction to the support move more fast than those with strong attraction. This is how the components are separated.

(iii) **Elution from the column.** After the sample is displaced or flushed from the stationary phase, the different components will elute from the column at different times. The components with the least affinity for the stationary phase (the most weakly adsorbed) will elute fast, while those with the greatest affinity for the stationary phase (the most strongly adsorbed) will elute last.

(iv) **Detection.** As different components emerge from the column they are collected. A detector analyzes the emerging stream by measuring a property which is related to concentration and characteristic of chemical composition. For example, the refractive index or ultraviolet absorbance is measured.

(v) **The chromatogram.** As the sample is separated in the column, different peaks on the chromatogram correspond to different components in the sample mixture. The chromatogram gives following informations :

- (i) *The level of complexity of the sample is indicated by the number of peaks which appear.*



- (ii) *Qualitative information* about the sample composition is obtained by comparing peak positions with those of standards.
- (iii) *Quantitative assessment* of the relative concentrations of components is obtained from peak area comparisons.
- (iv) *Column performance* is indicated by comparison with standards.

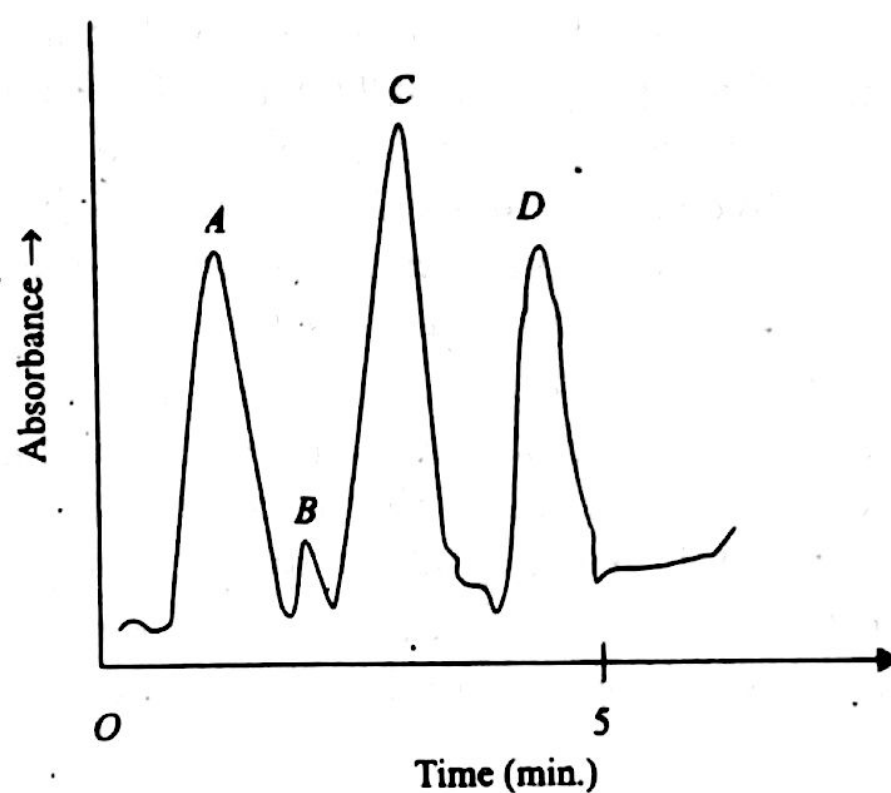
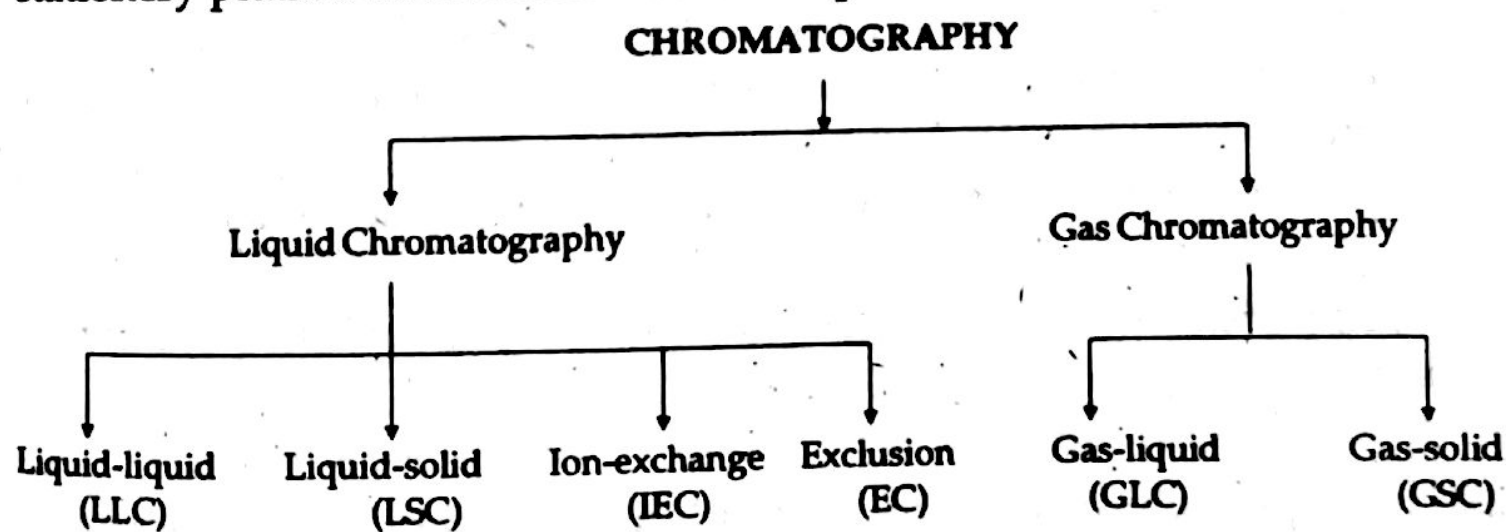


Fig. 20

## 8.2 Classification of Chromatography Methods

Chromatographic methods can be classified on the basis of types of mobile & stationary phase and the mechanism of separation.



In *Liquid-liquid chromatography (LLC)*, separation involves predominantly a simple partitioning between the immiscible liquid phases, one stationary & the other mobile.

In *Liquid-solid (or adsorption) chromatography (LSC)*, the stationary phase is solid and the mobile phase is liquid. The retentive ability of the stationary phase is due to the physical surface forces.

In *Ion-exchange chromatography (IEC)*, counter ions of the stationary phase are selectively exchanged with the ionic components of the sample.

In *Exclusion chromatography (EC)*, solute molecules are separated based on molecular geometry & size. Here stationary phase has porous, gel structure which is used in the form of exclusion packings.

In Gas-liquid chromatography (GLC), the mobile phase is a gas & stationary phase is a liquid and

Gas-liquid chromatography (SC), the mobile phase is a gas & stationary phase is a solid.

### 8.3 Gas Chromatography

Gas chromatography is so called because the mobile phase is a gas. It is of two types, viz. Gas-liquid chromatography (GLC) and Gas-solid chromatography (GSC); depending on whether the stationary phase is a liquid (held on a solid support) or solid respectively. Thus for GLC the stationary phase is a high-boiling liquid & the sorption process is predominantly one of partition. For GSC the stationary phase is a solid and adsorption plays the major role.

*Principle*: When the vapours of sample in a gas stream are allowed to pass through a column containing a stationary liquid or solid phase. Components of mixture migrate at different rates due to differences in boiling point, solubility or adsorption leading to separation of mixtures in microgram quantities.

*Apparatus & Instrumentation*: A gas chromatography consists of following important components regulator, injection port, glass or fused quartz column thermostated detector and recorder.

These components are joined together to:

- (a) Provide a constant flow of mobile phase (i.e., carrier gas),
- (b) permit the introduction of sample vapours into the flowing mobile phase,
- (c) contain the sufficient length of the stationary phase,
- (d) maintain the column at the appropriate temperature,
- (e) detect the sample components when they elute out from the column, and
- (f) provide a readable signal proportional in magnitude to the amount of each component.

These components (or better known as instrument modules) are shown schematically in Fig. 21.

#### Theory

Volatile samples which are thermally stable at the operating temperature are introduced into the gas stream via an injection port. Different constituents migrate at different rates due to their different distribution ratios between the mobile phase & stationary phase. A continuous flow of gas elutes the components from the column in order of increasing distribution ratio from where they pass through a detector connected to a recording system.

Generally, a chemically inert carrier gas is employed like He, N<sub>2</sub>, Ar or H<sub>2</sub>. The temperature of the separating column must be equal to or slightly above the average boiling point of the least volatile component of the sample. A good stationary phase is thermally stable & chemically inert. It has low volatility and good degree of compatibility with analytes. Generally, thermal conductivity detector, flame ionisation detector or electron capture detectors are used as they have

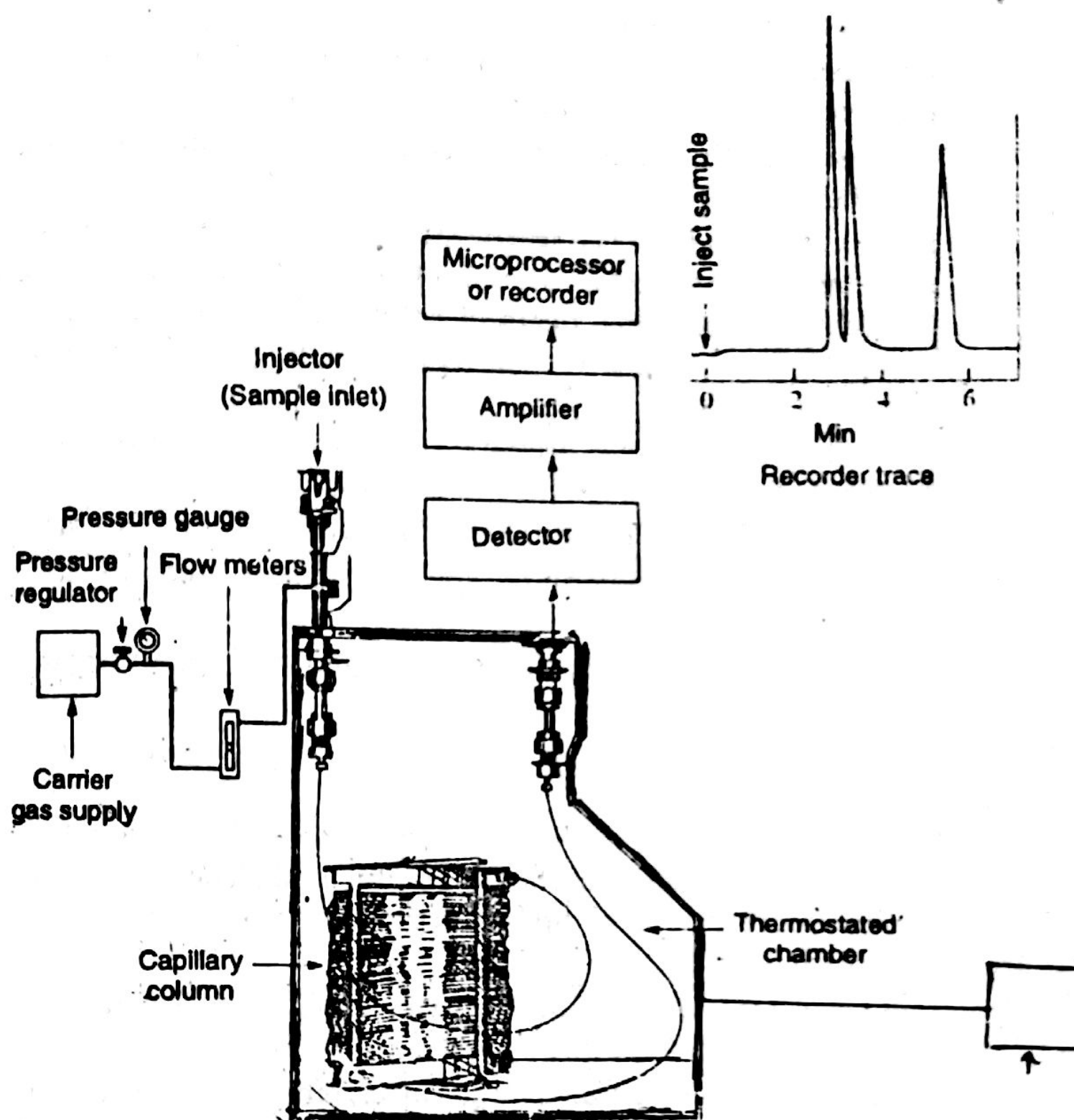


Fig. 21. Schematic diagram of a gas chromatography.

good precision and accuracy, high signal to noise ratio. They are non destructive and exhibit good response over a wide range of temperature. Detectors are selected according to carrier gas. For example, due to high thermal conductivity of He, thermal conductivity detectors are preferred for He. Ultimate accuracy of the chromatogram depends on the choice of detector recorder which is fed by the output of the detector. The availability of versatile and specific detectors and the possibility of coupling the gas chromatograph to an infra-red spectrometer or a mass spectrometer further enhance the usefulness of gas chromatography.

Gas chromatography is a unique & versatile technique. It is used not only for the qualitative identification of components in a sample, but also for the quantitative measurements (so it is an *Analytical Technique*). Once the analytical conditions have been determined the system may be scaled up to separate & collect gram amounts of components (so it is a *Preparative Technique*). It may also be used to investigate various parameters of a system, such as determination of partition coefficients, thermodynamic functions, and the adsorption isotherms (hence is also a *Physical Research Technique*)



### Application of Gas chromatography

- (i) Gas chromatography is used for the separation of thermally stable and volatile organic and inorganic compounds ;
- (ii) It is used for the analysis of gaseous samples, liquid solutions, and volatile solids ;
- (iii) It may be used to (a) study structure of chemical compounds, (b) determine the mechanisms and kinetics of chemical reactions, and (c) measure isotherms, heats of solution, heats of adsorption, free energy of solution and (or adsorption, activity coefficients, and diffusion constants) ;
- (iv) It can be used for the preparation of pure substances or narrow fractions as standards for further investigations ;
- (v) On an Industrial scale, it can be utilized for process monitoring ;
- (vi) It can be used to determine specific surface areas in adsorption studies ;
- (vii) Recently it has been utilized for elemental analysis of organic components, etc. .

A few examples of the applications of gas chromatography in various fields we summarized below :

(A) *Foods*. Analysis of fruit juices, wines, beers, cheeses, beverages, oils, dairy products is an active part of the gas chromatographic field. The determination of antioxidants, food preservatives, decomposition products, contaminants and adulterants are routinely done.

(B) *Drugs and Pharmaceuticals*. For quality control, analysis and monitoring (of metabolites in biological system).

(C) *Environmental Studies*. Asthma, lung cancer, emphysema, bronchitis and other chronic respiratory diseases could result from air pollution. Air samples can be very complex mixtures, and gas chromatography is easily adapted to the separation and analysis of such mixtures.

(D) *Petroleum Industry*. Gas chromatography is successfully used for the separation and determination of many components in petroleum products.

(E) *Clinical Chemistry*. Blood, Urine and other biological fluids can be analyzed for proteins, carbohydrates, amino acids, fatty acids, steroids, triglycerides, vitamins barbiturates either directly or after preparation of appropriate volatile derivatives.

### Advantages of Gas Chromatography

(a) *Versatility*. Gas chromatography is easily adapted for analysis of volatile solids, high-boiling liquids or samples of permanent gases.

(b) *Convenience*. It is easy to train non-technical personnel to carry out routine separations because of relatively straight forward procedure of gas chromatography.

(c) *Costs*. Compared to many other analytical instruments available today, gas chromatography are not too costly.

(d) *Analysis time*. It may range from several seconds to 30 min for the separation of all the components in a sample. This is due to the high diffusion rates in the gas phase & the rapid equilibrium between the moving and stationary phases.

(e) *High separating power.* Due to the low viscosity of mobile phase, very long columns with excellent separating power can be employed.

(f) *Sensitivity.* The sample size used is of the order of 1  $\mu\text{L}$  or less. Because of this high sensitivity, gas chromatography finds extensive uses.

(g) *Resolution.* It is possible to separate molecules that are very similar physically and chemically by this technique. Even the components that form a zeotropic mixtures in ordinary distillations may be separated by gas chromatography.

(h) *Assortment of sensitive detecting systems.* Detectors for gas chromatography possess rapid response rates, are relatively simple & highly sensitive.

(i) *Ease of recording data.* Output from detector in gas chromatographs can be conveniently interfaced with recording potentiometers, integrating systems, computers, and a wide variety of automatic data storing modules.

(j) *Automation.* Gas chromatography can be used for automatic monitoring of various chemical processes in which samples may be periodically taken & injected onto a column for separation and detection.

(k) *High relative precision.* It is of the order of 2-5%

### Disadvantages of Gas chromatography

(a) It requires that samples must be volatile & thermally stable below  $400^\circ\text{C}$ .

(b) Most commonly used detectors are non-selective,

(c) Published retention data are not always reliable for qualitative analysis.

## 9 ELECTRON SPIN RESONANCE SPECTROSCOPY (ESR)

It is a branch of spectroscopy in which microwaves induce transitions between magnetic energy levels of atoms or molecules having unpaired electron (s).

The energy levels are produced by the interaction of the magnetic moment of an unpaired electron in a molecule ion with an applied field. The ESR spectrum results due to the transitions between these energy levels by absorption of radiations having frequency in the microwave region.

The energy of the ESR transition is  $E = h\nu = gB_0 \frac{eh}{4\pi m_e c}$

where  $B_0$  is the applied magnetic field,

$m_e$  is the mass of electron,

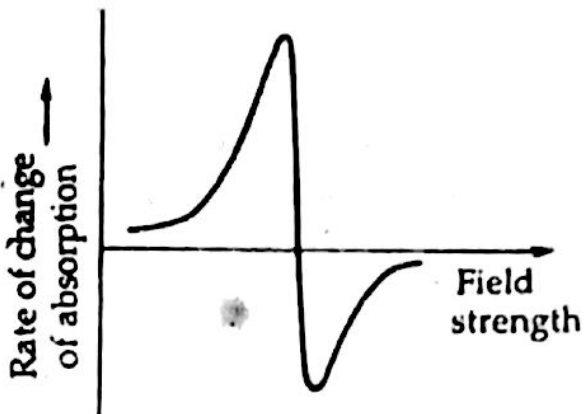
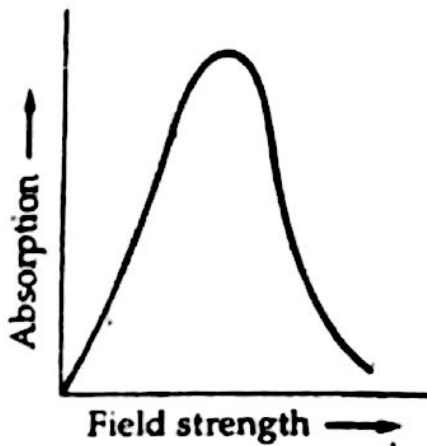
$e$  is the charge on electron,

$c$  is the speed of light and

$g$  is proportionality constant

which is a function of electron's environment and hence the orientation of the molecule having the unpaired electron w.r.t. applied magnetic field.

## 9.1 Comparison between NMR and ESR

S.No.	ESR	NMR
1.	Energy needed to induce transitions between magnetic energy levels of unpaired electron lie in the microwave region of the electromagnetic spectrum.	Energy needed to induce transitions between magnetic energy levels of $^1\text{H}$ nuclei in the radio frequency region.
2.	6.34 T is commonly used field strength.	Commonly used field strengths are 1.4, 2.3 or 14.1 T.
3.	ESR signals are a plot of the rate of change of absorption against field strength. 	NMR signals are a plot of absorption against field strength. 
4.	A radical has only one unpaired electron, and therefore, gives only one signal (split by coupling)	A molecule contains several $^1\text{H}$ nuclei and give rise to several signals (usually split by coupling).
5.	Sensitivity of ESR detection is very much higher than in NMR this is due to the very high magnetic moment of unpaired electron. (about 900 times that of the proton).	Sensitivity of NMR detection is very much lower than in ESR.

## 9.2 Hyper Splitting

Unpaired electron has magnetic moment which can interact with magnetic nuclei and leads to splitting of the ESR signal. When there are  $n$  number of magnetic nuclei present in a molecule, which can interact with electron, then  $(n + 1)$  signals are observed in the ESR spectra.

Splitting is measured in dimensions of Hz, represented by  $a_H$  and is called *hyperfine splitting*.

For example, (i) *Hydrogen atom*. Hydrogen atom shows two signals in ESR spectra. Hydrogen atom has one proton and one electron with spin ( $S = 1/2$ ). In the absence of a magnetic field electron gives doubly degenerate spin energy state. The degeneracy is removed when a magnetic field is applied. Two energy levels are created, one aligned with the field and other opposing the field. Each energy state is further split up into two energy levels. Four different energy states are thus obtained corresponding to two energy levels. Thus, there are two transition possible (shown by arrows) and ESR spectrum of hydrogen consists of two peaks.



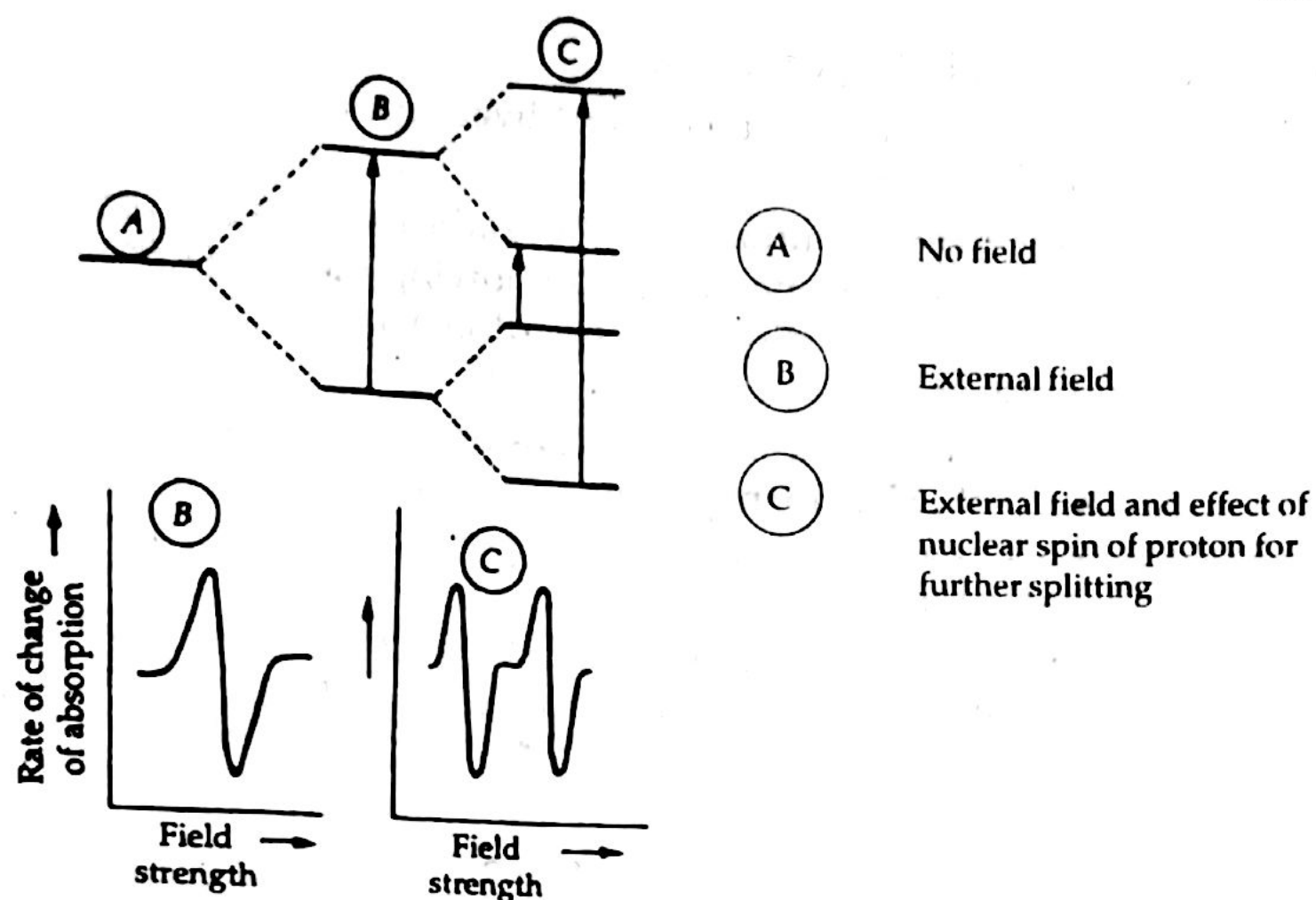


Fig. 22. (ESR Spectrum of hydrogen atom).

(ii) *Methyl radical* ( $\text{CH}_3$ ). It has one unpaired electron and three protons. As  $n = 3$  so ESR spectrum contains  $(3 + 1 = 4)$  equally spaced lines, i.e., a quartet.

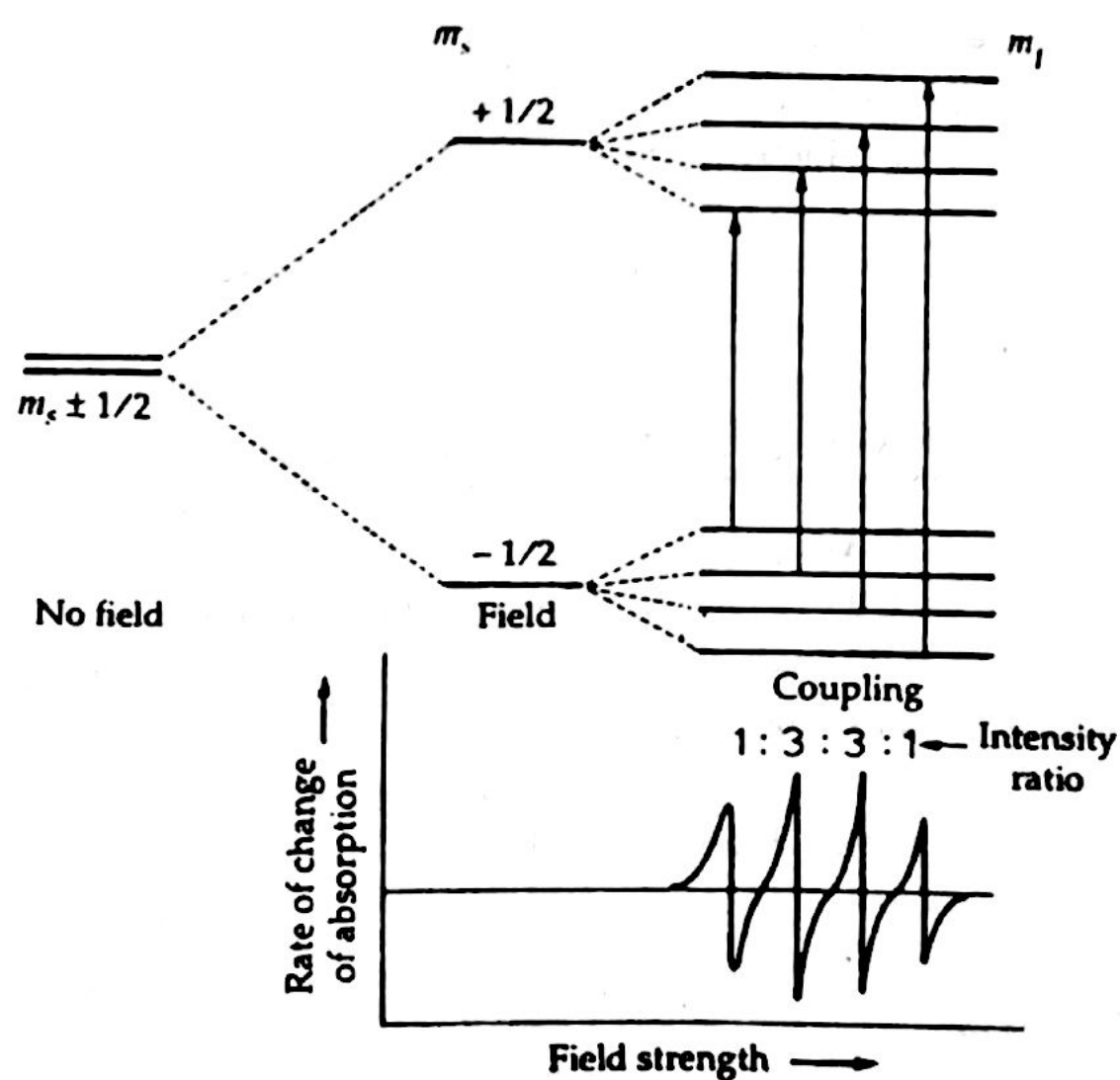


Fig. 23. ESR spectrum of Methyl radical.

**9.3 Application of ESR spectroscopy**

- (i) Detection of extremely short-lived free radical intermediates in chemical reactions.
- (ii) Relative concentrations of free radicals produced under different conditions can be measured by knowing the fact that the intensity of an ESR signal is directly proportional to the number of free radicals present.
- (iii) Identification of unknown ions and radicals is also possible with the help of ESR since hyperfine structure is a characteristic property of an ion or radical. It is a kind of finger print that helps to identify the free radicals present in the sample.
- (iv) ESR can also be used for the study of structure of proteins or other macromolecules by attaching spin labels, *i.e.*, those groups which have unpaired electrons.

**Exercises**

1. Briefly explain Vibrational Spectroscopy.
2. Discuss brief introduction of Electronic Spectroscopy.
3. What is the origin of vibration and electronic spectroscopy? In which spectral ranges these spectra occur?
4. Differentiate vibrational (or IR) and electronic (or UV) spectroscopy.
5. What is meant by vibrational and electronic spectroscopy? Discuss their origin and application in chemical analysis.
6. Explain Beer-Lambert Law.
7. What do you understand by 'molecular spectroscopy'? Name the different types of molecular spectra. In which region of the electromagnetic spectrum are they obtained?
8. Discuss the origin of nuclear magnetic resonance spectroscopy.

**R.G.P.V. Examination Questions**

1. Explain briefly the following :
  - (a) Beer-Lambert's law
  - (b) Applications of IR spectroscopy
  - (c) Applications of UV spectroscopy.
2. Explain briefly any four of the following :
  - (a) Beer-Lambert's law
  - (b) NMR spectroscopy
  - (c) Various techniques of chromatography
  - (d) IR spectroscopy
  - (e) Applications of UV spectroscopy.
3. Write short notes on :
  - (i) Calorimeter
  - (ii) Chromatography and its significance
  - (iii) IR spectroscopy
  - (iv) UV spectroscopy.

[Feb. 2005, 15 marks]

[Dec. 2003, 20 marks]

[Dec. 2002, 20 marks]

4. Write short notes on :

- (i) Beer and Lambert's law
- (ii) GLC
- (iii) UV spectroscopy
- (iv) IR spectroscopy.

5. (a) Write explanatory note on gas chromatography.

[June 2002, 20 marks]

(b) Point out the true and false statements out of the following :

- (i) Ultraviolet technique helps in predicting the number of conjugated double bonds in a molecule.
  - (ii) The substance which absorbs in the visible region appears coloured to the human eye.
  - (iii) Spectroscopy involves the interaction between matter and electromagnetic radiation.
  - (iv) In NMR, radiation of radio frequency range is used.
  - (v) In infra-red, electron-donating groups lower the wave number of absorption ; while the electron, attracting groups raise the wave number.
  - (vi) Chromatography is a technique which is not employed for the isolation, separation and identification of the components of a mixture.
- (c) Define the following forms :
- (i) Chromophore
  - (ii) Auxochrome
- (d) Describe briefly the theory of nuclear magnetic resonance spectrometry.

[May 2001, 20 marks]

6. Write short notes on any two of the following :

- (i) Chromatography and its applications,
- (ii) Beer-Lambert law,
- (iii) IR spectroscopy and its applications,
- (iv) UV spectroscopy and its applications.

[June 2003, 20 marks]

7. (a) Explain Beer-Lambert's law.

(b) Give a schematic diagram for a typical IR spectrometer.

(c) Describe the principle of NMR spectroscopy.

[June 2004, 20 marks]



## Cements

*"Health is the primary requisite for all activities : physical, intellectual and spiritual".*

### 1 INTRODUCTION

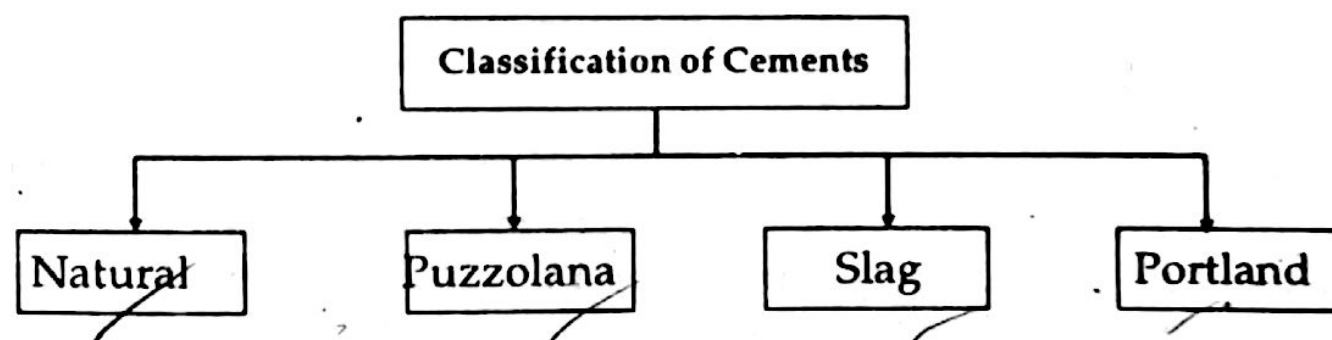
In this industrial age, the concrete is the most widely used non-metallic material of construction. It is used for the construction of buildings, bridges, high ways, dams, run-ways for the aircraft etc. The essential bonding material, which binds sand and rock (when mixed with water) in concrete is cement. In this chapter we will discuss cement (its classification, composition, manufacturing methods and decay), lime, plaster of paris and their setting and hardening.

### 2 CEMENT AND ITS CLASSIFICATION

Cement is a material which possesses adhesive and cohesive properties and capable of binding materials like bricks, stones, building-blocks etc.

#### Classification of Cements

There are four types of cements viz. Natural, Puzzolana, Slag and Portland cement. These are briefly discussed below :



#### (a) Natural Cement

**Preparation.** It is made by calcining a naturally occurring argillaceous limestone at a high temperature and subsequently, pulverizing the calcined mass. Calcium silicates and aluminates are formed by the combination of silica and alumina with calcium oxide during calcination.

#### Properties :

- (i) It possesses hydraulic qualities,
- (ii) It is quite setting cement, and
- (iii) It possesses relatively low strength.

#### Applications :

- (i) Mortars (combination of sand with natural cement) is used in laying bricks and setting stones.
- (ii) It is also used in large masses of concretes such as dams and foundations.

(b) **Puzzolana Cement.** It is oldest cement invented by Romans. It was used by them in making concrete for the construction of walls and domes.

✓ **Preparation:** This is made by mixing and grinding of natural puzzolana and slaked lime. (Natural puzzolana is deposit of volcanic ash produced by rapid cooling of lava. Lava in turn is a molten mixture of silicates of calcium, iron and aluminium.)

Puzzolana cements form hydraulic cementing materials.

**Properties.** They also possess hydraulic properties.

**Applications.** They are first mixed with portland cements and then used for different applications.

### (c) **Slag Cement**

**Preparation.** It is made from hydrated lime and blast furnace slag. A mixture of calcium and aluminium silicates (i.e., blast furnace slag) is granulated by pouring it into a stream of cold water. Subsequently, it is dried and mixed with hydrated lime. Then the mixture is pulverized to fine powder. Sometimes, accelerator like clay, salt or caustic soda are added to hasten the hardening process.

**Properties :**

- (i) Slag cements are slow setting,
- (ii) They are poor in abrasion-resistance and
- (iii) They have lower strength.

**Applications.** Because of the above shortcomings, slag cements have very limited applications. It is used for making concrete in bulk construction.

(d) **Portland Cement.** It is made by calcining (at about 1500°C) an intimate and properly proportioned mixture of clay and lime containing raw materials. After calcination, retarder like gypsum is added.

It is discussed in detail in the following sections.

## 3 **PORTLAND CEMENT**

Portland cement is also known as "magic powder". It consists primarily of compounds of lime, silica, alumina and iron. It forms a paste when mixed with water. This paste subsequently hardens and binds the aggregates (crushed rock, sand, gravel, etc.) together to form a hard durable mass called concrete. Thus, cement is one ingredient of concrete.

*William Aspdin is generally recognized as the father of the modern portland cement industry.* Because in 1824, he produced an improved cement by heating a mixture of limestone and clay and crushing the resulting product to a fine powder. The name portland cement was used because this powder, on mixing with water, set to give a hard, stone-like mass which resembled stone quarried on the Isle of Portland, England.

Portland cement is a type of cement, not a brand name. Each cement manufacturer makes portland cement. All portland cements are *hydraulic cements* because they set and harden under water.

### 3.1 **Manufacture of Portland Cement**

**Raw Materials.** Raw materials required for the manufacture of Portland cement may be divided into those supplying

(a) *The lime (CaO) component* (i.e. calcareous materials such as Aragonite, Calcite, Marl, Shale and limestone) ; (b) *The silica (SiO<sub>2</sub>) component* (i.e., siliceous materials such as clay, marl, shale and sand) ; (c) *The alumina (Al<sub>2</sub>O<sub>3</sub>) component* (i.e., Argillaceous materials such as alumini-um-ore refuse, caly, fly ash and shale) ; (d) *The iron (Fe<sub>2</sub>O<sub>3</sub>) component* (i.e. Ferriferous materials such as clay, iron ore, mill scale etc.)

**Manufacturing process.** The manufacture of portland cement involves the use of skills of engineers, chemists and technicians to ensure a uniform product. The actual manufacturing involves the following operations :

(i) **Crushing.** It is done in primary crusher (which reduces the size of limestone to an approximately 5-in) and in secondary crusher (it further reduces the size to 3/4-in).

(ii) **Mixing.** It begins with the acquisition of raw materials such as limestone, sand and clay. These are mixed either by the dry process or by the wet process. The raw materials which are stored in the bins are first proportioned and then delivered to the grinding mill. The *dry process* produces a fine ground powder. It is stored in bins. The *wet process* (in the presence of water) results in a slurry, which is mixed and pumped to storage basins.

(iii) **Burning.** Both dry and wet processes feed rotary kilns where burning results in actual chemical changes. The rotary kiln is a long steel cylinder with length 30-160 metres and diameter 2-4 metres. Its inside surface is lined with fire brick refractory. It is slightly inclined downwards towards the exist end. It can be rotated at desired speeds as it is mounted on rollers. The material is fed in the rotary kiln from the upper end. As the kiln rotates, the material passes slowly from the upper to the lower end at a rate controlled by the slope and speed of rotation of the kiln. The kiln is heated (using solid, liquid or gaseous fuel) from the lower end. The upper end is cooler. As the material passes through the kiln, its temperature is raised to the point of clinkering temperature where the actual chemical reactions take place. In fact, there are different zones in the rotary kiln, viz.

**Table 1. Pros and Cons of dry and wet Processes**

Dry Process	Wet Process
1. It is a slow and costly process.	It is comparatively faster and cheaper process.
2. Cost of production of cement is less, as the fuel consumption is low. Shorter kiln is sufficient.	Cost of production is somewhat higher because of the higher fuel consumption. As longer kiln is needed to drive off the excess water.
3. The quality of cement produced is inferior.	The quality of cement produced is somewhat superior, as more accurate control of composition can be attained.
4. This process is adopted when the raw materials are quite hard.	This process is preferred when the raw materials are soft.
5. This process is not suitable when the principal raw material has an inherent moisture content of 15% or more, as it is uneconomical to drive away the excessive quantity of moisture.	This process has to be adopted in this case.



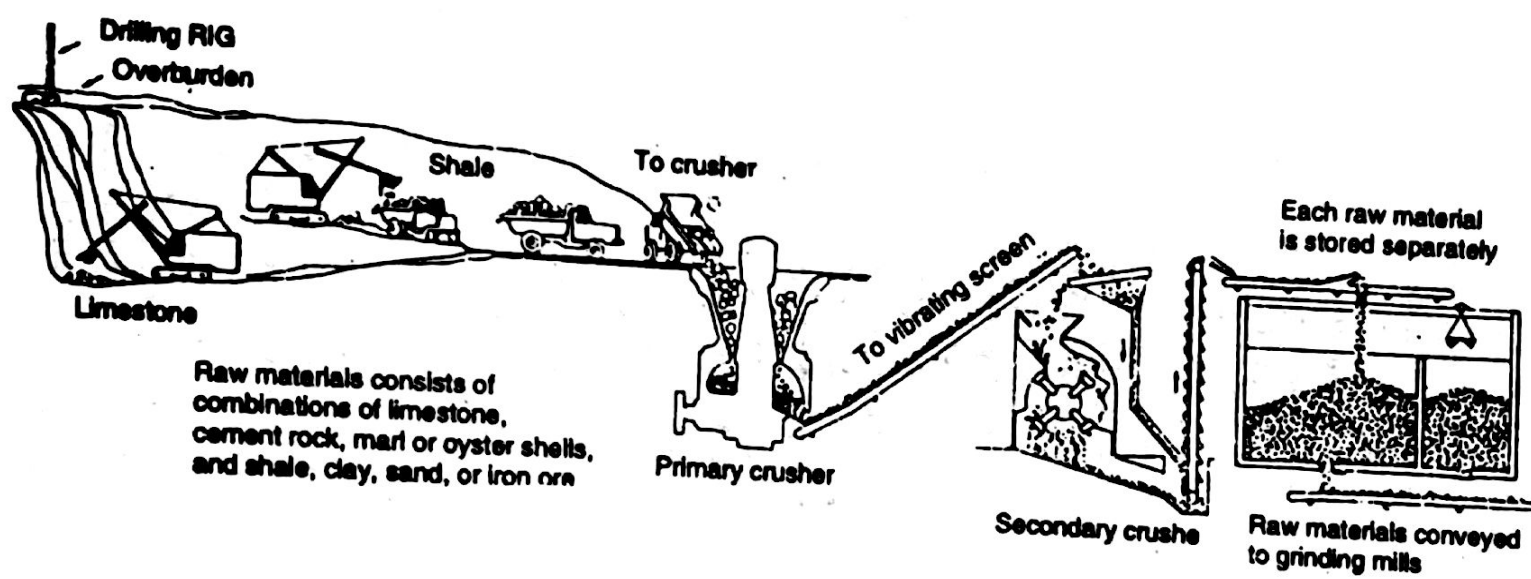


Fig. 1. (a) Crushing : stone is first reduced to 5-in. size, then 3/4-in. and stored.

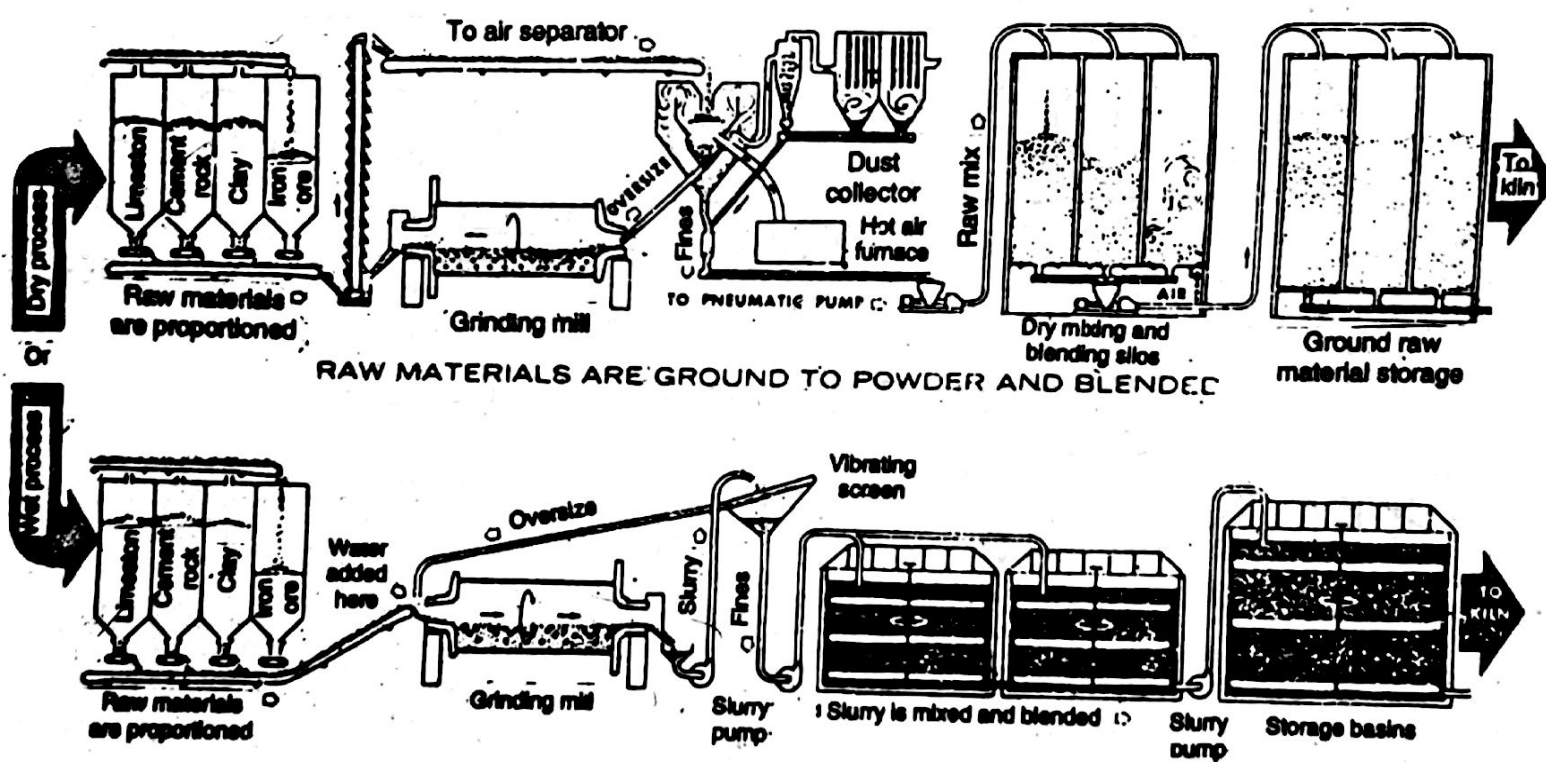


Fig. 1. (b) Mixing : (Raw material are ground, mixed with water to form slurry and blended).

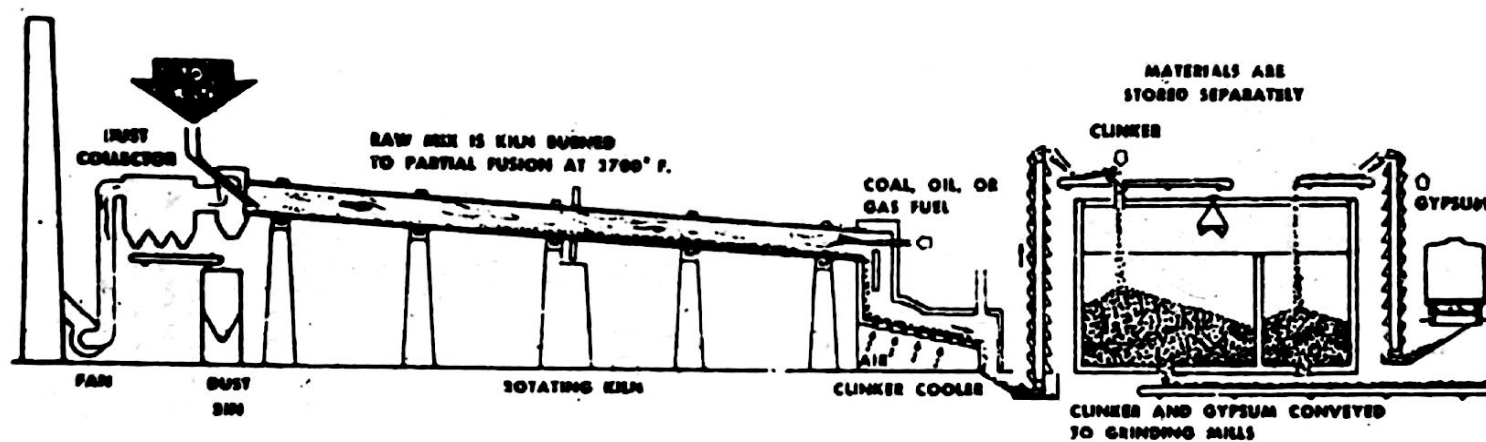


Fig. 1.. (c) Burning : Burning changes raw mix chemically into cement clinker.

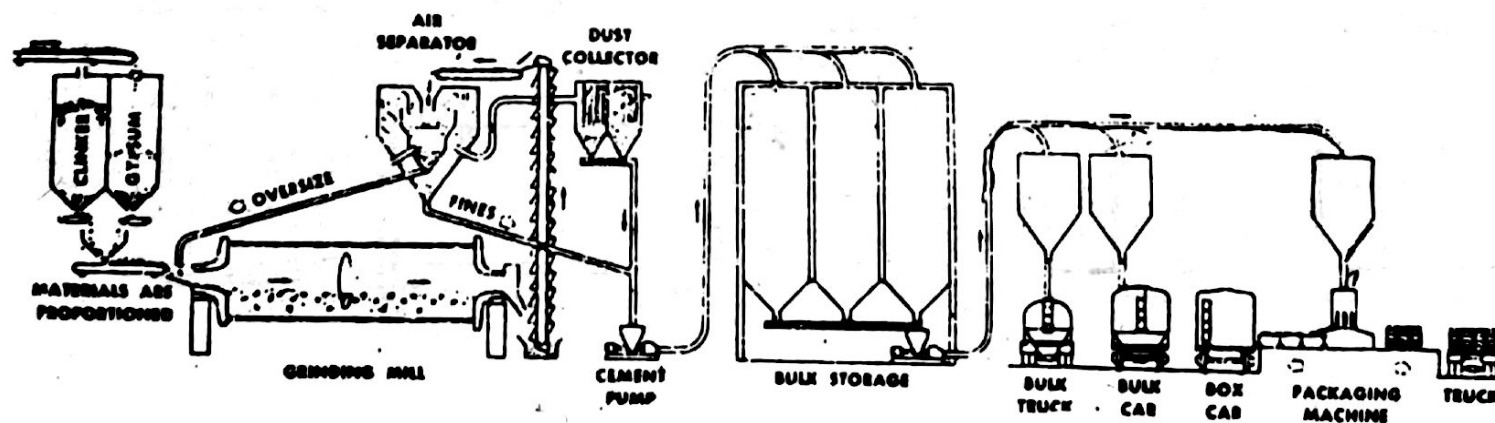
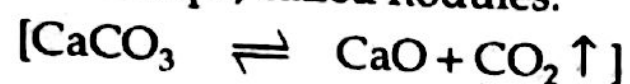


Fig. 1. (d) Grinding : Clinker with gypsum added is ground into portland cement and shipped.  
Manufacture of portland cement.

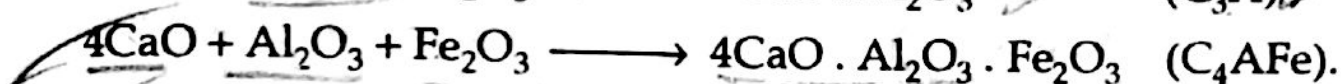
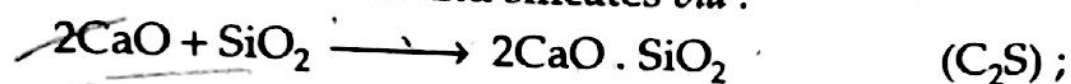


(a) *The drying zone.* Here the temperature is moderate (100–500 °C) and this zone is located at upper one-fourth of the length of the kiln. This zone is known as drying zone, because the moisture is driven out and the materials get heated.

(b) *Calcination zone.* Its temperature is about 1000 °C and it is the middle portion of the kiln. In this zone, CO<sub>2</sub> is expelled from lime-stone, quick-lime (CaO) is formed in the form of small lumps, called nodules.



(c) *Burning Zone.* Its temperature is about 1400 – 1500 °C and is the bottom and hottest portion of the kiln. In this zone, mixture melts and forms little rounded pasty masses of about the size of the peas which are called *clinkers*. The clinker produced is greenish black or black in colour and has rough textured. Its size makes it relatively inert in the presence of moisture. In this zone, lime and clay undergo fusion yielding calcium aluminates and silicates *via* :



(iv) *Grinding.* From clinker storage the material is transported to final grinding where it is ground to the requisite fineness according to the class of the product. Finely ground clinker sets very fast by absorption of moisture from the atmosphere.

(To control the setting time of the portland cement (when it is mixed with water) approximately, 2 to 3% gypsum (CaSO<sub>4</sub> · 2H<sub>2</sub>O) is added.)

(The mixture of clinker and gypsum powder is known as portland cement). It is stored in silos from which it is bagged or loaded for shipment.

The flow diagram for the manufacture of portland cement is shown in Fig. 2.

#### Notes :

- ✓ The portland cement will retain its cementing quality until it comes in contact with moisture. Hence, it should be stored in a dry and airtight location.
- When bagged cement is in storage for long durations it sometimes acquires a 'warehouse pack'. This can usually be corrected by rolling the bag on the floor.
- ✓ Portland cement should be free of lumps and free flowing when used. It is advisable not to use a cement which contains lumps that cannot be easily broken up.

### 3.2 Chemical Composition of Portland Cement

Portland cements are composed of following four basic chemical compounds :

S. No.	Name	Chemical formula	Abbreviation
1.	Tricalcium silicate	3 CaO SiO <sub>2</sub>	C <sub>3</sub> S
2.	Dicalcium silicate	2 CaO SiO <sub>2</sub>	C <sub>2</sub> S
3.	Tricalcium aluminate	3 CaO Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A
4.	Tetracalcium aluminoferrite	4 CaO Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub>	C <sub>4</sub> AFe

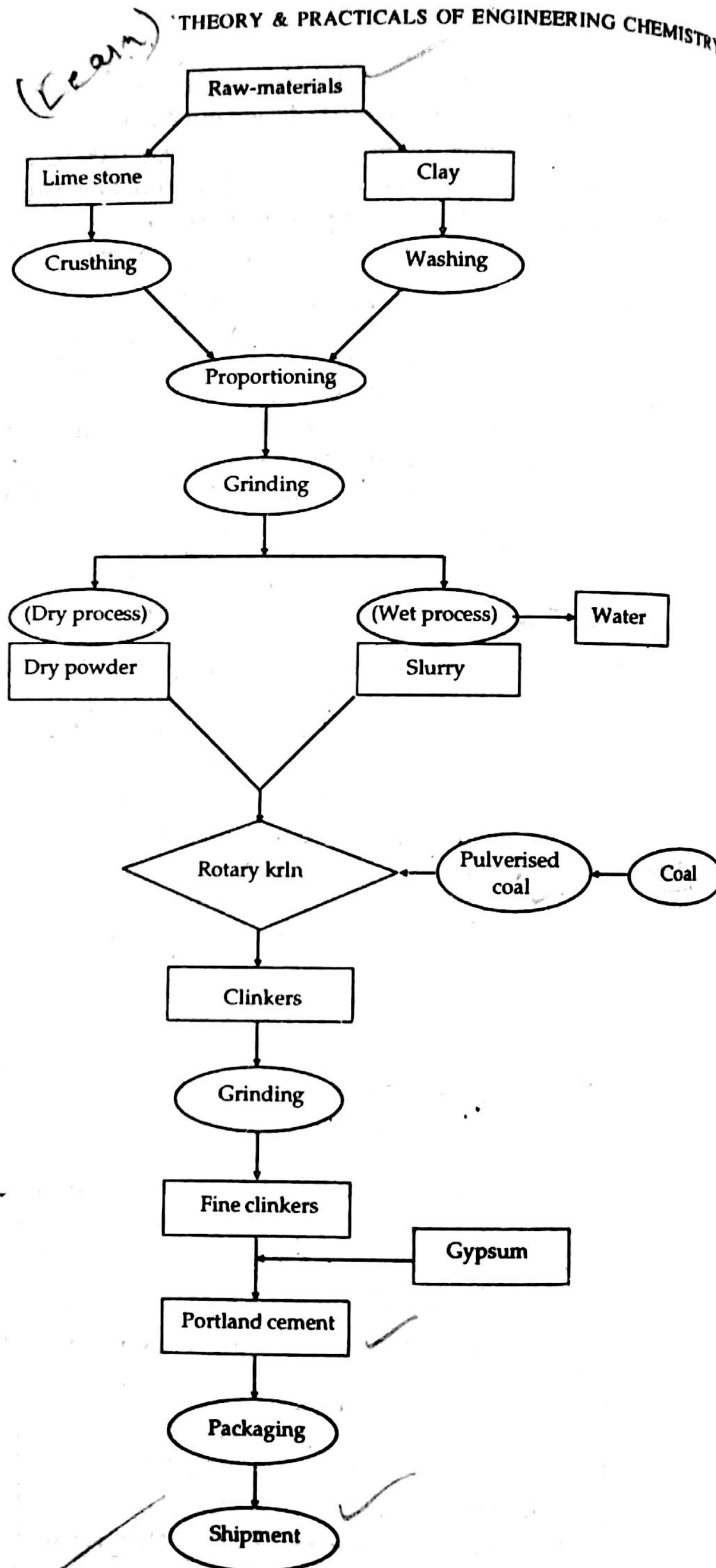
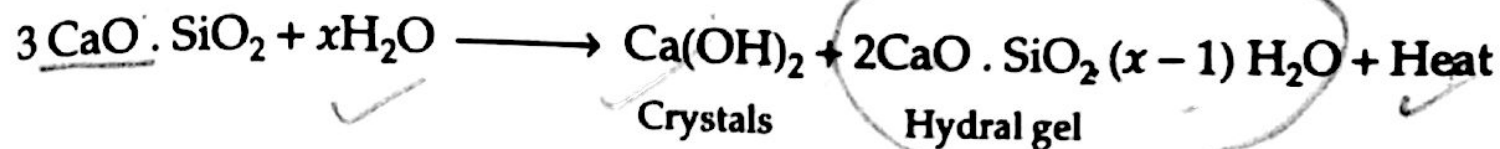


Fig. 2. Flow diagram for the manufacture of portland cement.

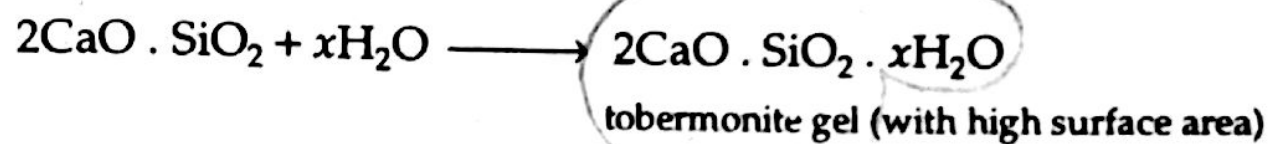
The behaviour of the cement can be altered by modifying the relative percentages of these compounds, as each of the components exhibits a particular behaviour.

Tricalcium silicate ( $C_3S$ ). It is largely responsible for initial set and early strength as it hardens rapidly as per the reaction shown below :



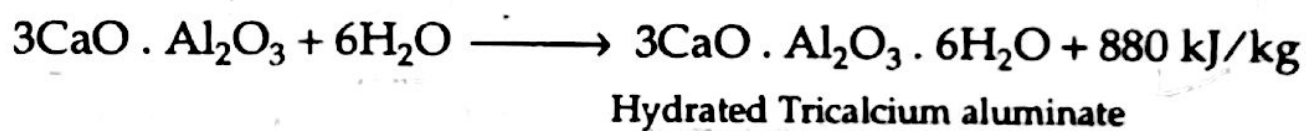
The hydral gel thus formed is responsible for the binding action between the aggregates.

Dicalcium silicate ( $C_2S$ ) hardens slowly, and its effect on strength occurs at ages beyond one week. This is due to its slower rate of reaction with water



However, if moist curing is continued, the later strength after about 6 months will be greater for cements with a higher percentage of  $C_2S$ .

Tricalcium aluminate ( $C_3A$ ) is the first compound to hydrate and it contributes to strength development in the first few days.



The above reaction is highly exothermic. Cements made with low  $C_3A$  contents usually generate less heat, develop higher strengths, and show greater resistance to sulphate attacks. In general,  $C_3A$  is least desirable component because of (a) its high heat generation and (b) its reactivity with soil and water containing moderate to high sulfate concentrations.

The presence of gypsum in the cement helps to retard the speed of the initial set. This is due to the formation of calcium sulphoaluminate (by the reaction between gypsum and  $C_3A$ ) which does not show any tendency to rapid hydration.



The tetracalcium aluminoferrite ( $C_4AF$ ) compound assists in the manufacture of portland cement by allowing lower clinkering temperature. Even though it hydrates very rapidly, it contributes very little to the strength of concrete.



### 3.3 Setting and Hardening of Cement

(When water is mixed with cement paste to form a fluid paste, hydration of cement takes place. The mixture eventually becomes stiff and then hard. This process is known as setting.) After hydration, anhydrated compounds become



hydrated which have less solubility. Hence they are precipitated as insoluble gels or crystals. These have the ability to surround sand, crushed stones (in mortars or concretes) on other inert materials and bind them very strongly.

The physical changes occurring in the setting and hardening of cement may be summarized diagrammatically as follows :

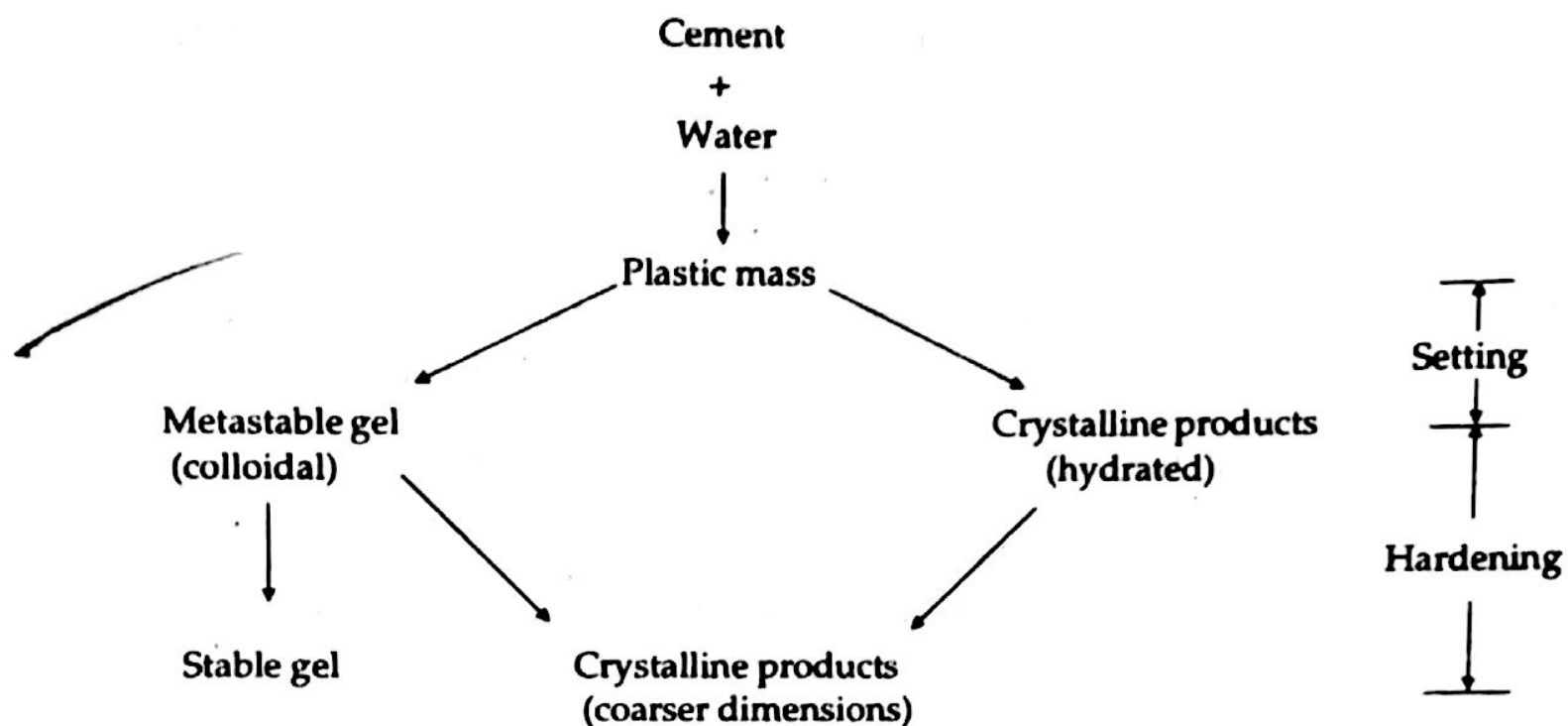


Fig. 3. Schematic diagram of setting and hardening of cement.

Hardening of cement can be explained on the basis of two theories :

(i) Colloidal theory (by Michaelis). According to this theory, during hydration silicate gels are formed which undergo hardening and are responsible for the hardening of cement.

(ii) Crystalline theory (by Lechatlier). According to this theory, constitutional compounds after hydration form crystalline products. These crystalline products undergo interlocking which is responsible for hardening of cement.

Thus, it can be concluded that setting and hardening of cement is due to the formation of interlocking crystals reinforced by the rigid gels formed by the hydration and hydrolysis of the constitutional compounds.

Stiffening of a concrete mixture with little evidence of significant heat generation is known as *false set*. Further mixing without additional water can restore plasticity in such cases.

In some cases, cement also exhibits a *flash set*. In these cases the cement has hydrated and further remixing will do no good.

• Most portland cements exhibit initial set in about 3 hours and final set in about 7 hours. If the cement sets too slowly valuable construction time would be lost. A cement used in concrete must not set too fast as it requires some time to be placed and finished. The rapid set makes the material unworkable.

The main constituents of cement, their percentage composition and characteristic property they impart to cement are summarized in Table 2 :

**Table 2 : The main constituents, their percentage composition and their Influence on the properties of portland cement**

S. No.	Cement Constituent	% range by mass	Functions
1.	Lime (CaO)	60-69	Too little lime reduces strength of cement if its content is high. It gives high early strength but generally increases the setting time. Too high a % of lime produces cement of unsound quality and makes it liable for disintegration.
2.	Silica (SiO <sub>2</sub> )	17-25	Its higher % increases the strength and usually prolongs the setting time. High silica cement do not attain their full strength for a considerable period.
3.	Alumina (Al <sub>2</sub> O <sub>3</sub> )	3-8	Its higher % increases the strength and reduces the setting time.
4.	Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	2-4	It imparts characteristic grey colour strength and hardness to the portland cement.
5.	Magnesium oxide (MgO)	1-5	
6.	Sulphur trioxide (SO <sub>3</sub> )	1-3	It imparts soundness to cement when present in small amount.
7.	Alkali Oxides (Na <sub>2</sub> O + K <sub>2</sub> O)	0.3-1.5	If present in excess, causes the cement efflorescent.

### 3.4 I.S.I. Specifications of Portland Cement

Specifications for ordinary portland cement as per Indian standard : 269-1975, are given below :

- (i) Lime saturation factor  $\left[ \frac{\text{CaO} - 0.7 \text{SO}_3}{2.8 \text{SiO}_2 + 1.2 \text{Al}_2\text{O}_3 + 0.65 \text{Fe}_2\text{O}_3} \right]$   
= 0.66 to 1.02
- (ii) The ratio  $\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$  shall not be less than 0.66
- (iii) Insoluble residue should not exceed 2%
- (iv) The weight of magnesia (MgO) : should not exceed 6%
- (v) Total sulphur contents, calculated as sulphuric anhydride (SO<sub>3</sub>) shall not be more than 2.75%
- (vi) Loss on ignition shall not exceed 4%
- (vii) Fineness not to exceed 10%, after sieving the residue (by weight) on B.S. 170-mesh test sieve.
- (viii) Setting times : Initial = 30 minutes  
Final = 10 hrs.
- (ix) Heat of hydration :  
After seven days :  $\leq 65 \text{ cal/gm}$   
After twenty Eight days :  $\leq 75 \text{ cal/gm}$

(x) Compressive strength :

After three days :  $\geq 1600$  lb/sq. inch

After seven days :  $\geq 2500$  lb/sq. inch

(xi) Tensile strength :

After three days :  $\geq 300$  lb/sq. inch

After seven days :  $\geq 375$  lb/sq. inch

### 3.5 Physical Properties of Portland Cement

(i) *Fineness*. It affects the hydration of cement. For a given weight of cement, the surface area of the grains of a fine-ground cement is greater than for a coarse-ground cement. Hence, hydration process occurs more rapidly in a fine-ground cement as water is in contact with more surface area. The cement should not be ground too finely because there is a possibility of prehydration due to accidental contact with moisture vapour during manufacturing and storage. This results in loss in cementing properties of the material.

In general, the finer a cement is ground, the higher the heat of hydration and resulting accelerated strength gain.

(ii) *Soundness*. It is the ability of a cement to maintain a stable volume after setting. A sound cement resists cracking, disruption and eventual disintegration of the material mass. An unsound cement has excessive amounts of free lime which is enclosed in cement particles. After the cement has set, when the moisture reaches the lime, lime expands with considerable force, disrupting the set cement.

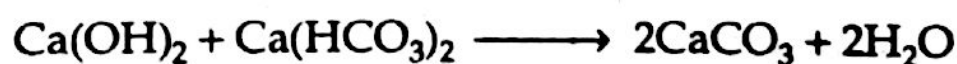
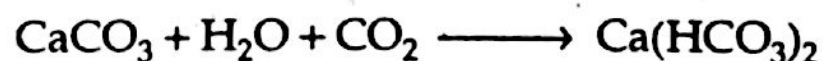
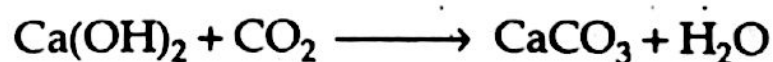
### 3.6 Decay of Cement

The cement constituents are susceptible to attack by salty water and other acidic solutions. When the surface is impermeable, then this rate of attack will be slow. However, structure can weaken and undergo deterioration on long exposure.

Acidic water can attack the cement structures. With decrease of pH (on increase of acidity), the rate of attack increases. Dissolved  $\text{CO}_2$  or presence of other organic and inorganic acids are responsible for acidity of water.

*Decay of cement is due to*

(i) the leaching out of free lime from it. This leaching is due to the chemical action of  $\text{CO}_2$  present in acidic water.



Initially, insoluble  $\text{CaCO}_3$  is formed, which is then dissolved out with further reaction with carbon dioxide and water leading to the formation of soluble calcium bicarbonate  $\text{Ca(HCO}_3)_2$ . Till there is consumption of all  $\text{CO}_2$ , this cycle of reaction continues.

(ii) Hydrolysis of silicates and aluminates, which will also be dissolved out.

*Prevention*. Decay of cement can be minimized by coating the surface with epoxy resin paint or bituminous or linseed oil (or other drying oils). This coating makes the surface impermeable to acidic water.

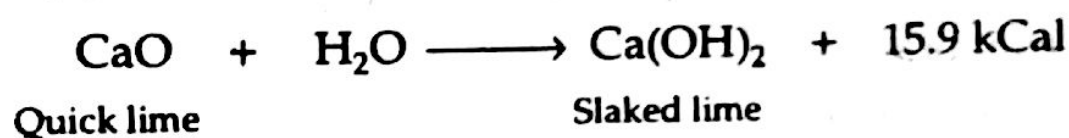


In the case of concrete pipes carrying sewage (which is normally alkaline), decay is due to the attack on the  $\text{SiO}_2$  component in the cement by these alkaline sewage. To overcome this, surface is treated with  $\text{SiF}_4$  when insoluble  $\text{CaF}_2$  is formed.

#### 4 LIME

It consists essentially of either calcium oxide ( $\text{CaO}$ ) alone or smaller proportion of magnesium oxide ( $\text{MgO}$ ) along with  $\text{CaO}$ . It is formed by burning limestone ( $\text{CaCO}_3$ ) at such a temperature that it will slake when brought in contact with water.

**Setting and hardening of lime (or lime-mortar).** When water is added to pure lime (also known as quick-lime), it is readily absorbed through the pores of the quicklime lumps and slaked lime [ $\text{Ca(OH)}_2$ ] is formed along with the considerable amount of heat.



This exothermic process is known as *slaking (or hydration)*. During slaking, water is converted into steam and lime is changed to a fine powder of  $\text{Ca(OH)}_2$ , called as *slaked lime*.

Manufacturers supply lime in the form of a fine white powder, obtained by adding a limited amount of water to lime. This partially slaked lime is known as *hydrated lime*, it can be used immediately, and is easier to handle and store. But when this is slaked, much less heat is evolved.

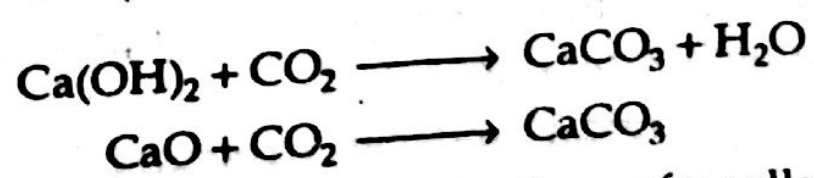
As such the lime paste is unsatisfactory as a cementing material. This is due to the fact that it shrinks and cracks on drying. Pure calcium limes are poorly plastic, rather sticky and hard to work. (Plasticity is the ability of lime to spread during application).

Thus lime is mixed with sand (in 1 : 3 ratio) (to form mortar or plaster) to decrease the shrinkage of lime on setting, to get a proper plastic mix and to decrease the cost. The addition of sand makes the mass more porous. Hence  $\text{CO}_2$ , which is essential for hardening of lime mortar can penetrate the structure to react with  $\text{Ca(OH)}_2$ .

The process of setting and hardening of lime (or lime-mortar) involves the following :

The lime mortar initially loses water by evaporation (Dehydration). It can also occur by absorption of water by porous bricks. A stiffening of mortar (setting results) but no strength is imparted.

On exposure to air, carbonation results which is the combination of atmospheric  $\text{CO}_2$  with lime ( $\text{CaO}$ ) or ( $\text{Ca(OH)}_2$ ), forming lime stone ( $\text{CaCO}_3$ ).



In the mortar part,  $\text{Ca(OH)}_2$  is in the form of a colloidal gel, which gradually hardens.

The hardening process is very slow, it takes months or even years. In this process, a hard coherent mass is formed as the  $\text{CaCO}_3$  crystals interlock the sand particles. In the matrix of the set mortar, the dispersed sand minimizes the development and propagation of cracks by presenting the heterogeneous phase during the hardening process.

*Setting of hydraulic lime* is mainly caused by the decomposition of complex silicates of calcium and aluminium into simpler compounds such as silicate aluminate and hydroxide of calcium. This decomposition takes place in presence of water. The so formed simple compounds crystallise to form a hard mass in the interior; while calcium hydroxide  $\{\text{Ca}(\text{OH})_2\}$ , which is soluble in water, comes to the surface. There it crystallizes to form calcium carbonate, under the action of atmospheric carbon dioxide. Due to this fact, hydraulic limes can set and harden under water also. A free circulation of air is beneficial for hardening, since it provides necessary  $\text{CO}_2$  and also removes the water formed in the hardening reaction by evaporation.

## 5 PLASTER OF PARIS

It is formulated as hemihydrate of calcium sulphate  $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$  (or  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and is believed to consist of a series of hydrates ranging from  $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  to anhydrous  $\text{CaSO}_4$ .

The commercially available plaster of paris is a mixture of the hemihydrate of calcium sulphate ( $\text{CaSO}_4$ ) and some unchanged gypsum.

*Preparation.* It can be prepared from gypsum (hydrated calcium sulphate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) by following unit operations:

- (i) crushing and grinding of gypsum;
- (ii) calcination of ground gypsum in kilns by heating to about  $150^\circ\text{C}$ ; and
- (iii) pulverizing the calcined product.

### Setting and hardening

Plaster of Paris forms a plastic mass when it is mixed with water. This plastic mass quickly sets or hardens. During this process, it slightly expands and regains the closely-packed crystalline structure of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

Alums or alkali sulphates ( $\text{K}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$  etc.) can initiate as well as hasten the crystallization process. Hence, they are used for accelerating the setting of plaster of paris.

### Applications of plaster of Paris

- (i) It is used for making moulds as it expands slightly on setting, details are thereby accurately reproduced.
- (ii) It is used in making surgical bandages, structural tiles and castings.
- (iii) It is also used for making plaster-board, which is made up of alternate layers of gypsum plaster and a fibrous material such as felt or paper.

## EXERCISES

1. (a) Explain the mechanism of setting and hardening of cement.  
(b) Explain in brief manufacture of Portland cement by wet process.
2. (a) Why Portland cement so-named?  
(b) Write short note on setting and hardening of lime.
3. (a) Discuss the role of gypsum in cement?  
(b) How are the cements classified.
4. (a) Give the important methods of manufacturing Portland cement and discuss the chemistry involved in the setting of cement.  
(b) Discuss the pros and cons of dry process over wet process.
5. (a) Draw a labelled diagram of rotary kiln. Write chemical reactions taking place in the various zones of rotary kiln.  
(b) Define Soundness of cement.
6. What are the constituents of Portland cement? Explain the role of each constituent.

## Examination Questions

1. (a) Write the chemical reactions involved in the manufacture of the Portland cement.  
(b) Why is Gypsum added to cement. [RGPV, B.E., 1<sup>st</sup> Sem., 2001]
2. How are the natural and puzzolana cements prepared? Name the raw materials used in the manufacture of portland cement and write their average composition in the final products. Discuss setting and hardening of portland cement.  
[J.M.I., B.Tech., Part-I, 2000]
3. Name the basic constituents of cement. What is their average percentage in the cement? Discuss their roles in attainment of strength of cement on its hydration.  
[J.M.I., B.Tech., Part-I, 2001]
4. Draw flow-diagram to show the various steps involved during portland cement manufacture by Rotary kiln technology. Also write the chemical reactions along with temperatures which occur during the process.  
[Univ. of Raj., B.E., 1<sup>st</sup> Sem., May 2001]
5. Draw a labelled diagram of rotary kiln used for the manufacture of portland cement by wet process and state its working. [Raj. Univ. 2002]
6. Write short notes on : Vertical Shaft Kiln (VSK) technology. [MREC, 2002]

(b) Gypsum is added to increase the setting time of the portland cement (when it is mixed with  $H_2O$ ) and is used as a retardant.